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Master thesis

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Influence of ultraviolet radiation on surface topography of PMMA material

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Influence of ultraviolet radiation on surface topography of PMMA material

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Abstract:

For the first time it was discovered that ultraviolet radiation with a wavelength of 200 to 400 nm (maximum 365 nm) radiated from a distance of 40 cm (intensity: 3500 mW/cm²) to PMMA altered its surface wettability as well as a roughness at the nanoscale that was observed with an atomic force microscope (AFM). The roughness rises and falls again in a short time (1-2days) after 75 min and 180 min irradiation time. However , during the next 10 days roughness became stabilized and there was no influence of UV if PMMA was stored in air or in a Petri dish out of glass.

Preface

Experiments for the following master thesis were done at Riga Technical University. After studying Engineering Physics with focus medical engineering at Hochschule Mittweida in Germany I went to a stay abroad to Riga/Latvia, which was organized by Erasmus.

Topic was part of a dissertation of Linda Lancere, her supervisor was Prof. Dekthyar.

Before this work I wrote a research project with the title " Influence of ultraviolet radiation on micro hardness of PMMA material " with the same experimental conditions, which was also a part of my curriculum in Mittweida. Also master thesis was a part of curriculum, so I had supervisors in Riga, Linda Lancere and Prof. Dekthyar and also a supervisor in Mittweida, Prof. Hinderer.

Thanks

I want to give thanks to all, who supported me to write this master thesis.

Especially I thank Prof. Yuri Dekhtyar and PhD student Linda Lancere from Riga Technical University for all the support in the experiments.

Furthermore I thank Prof. Ralf Hinderer from Hochschule Mittweida for all the help because of writing my master thesis in a foreign country and Prof. Fischer, who was my supervisor for consultation in Mittweida.

Thanks to international student´s offices of Riga Technical University and Hochschule Mittweida for help with the organization of my trip to Latvia and also to all professors and assistants, who taught me the knowledge I needed for this work.

Table of content

0 Introduction

0.1 Motivation

For a better tolerance of hard contact lenses and artificial eye lenses wettability of surface has to rise. PMMA is the oldest material for hard contact lenses after glass [NDR2014] and it is also used today. So the Hungarian company opto-centar reports that their hard contact lenses are made from PMMA [Oce2014] and also some shops in the internet sell these products [Ide2014]. On the other hand it is also reported by a German company, that contact lenses have made out of another not named material since 1980 [Ala2014]

Costly tests of biocompatibility can be avoided by using this well known material.

The idea of the project by Riga Technical University is to leave material the way it is and to change just the surface with ultraviolet radiation for a better wettability. This effect is losing with time, so it is not possible to irradiate directly after production.

The aim is, that user can buy contact lenses, put them under a UV lamp by himself, push a button and wait until lenses are irradiated to get a higher wettability and thus a better compatibility. Of course irradiation needs easy conditions, so irradiation has to happen in air conditions.

0.2 Topic

For this motivation all the other parameters have to be checked. One of the most important parameters of the surface is roughness that is observed in this thesis.

The surface of the contact lenses is in a direct contact to human eye and it could also have an influence to tolerance.

Because some contact lenses are worn for a longer time and artificial eye lenses are worn for a very long time it is important to know what happens after storage.

Storage conditions were also observed. For that as storage materials air and a Petri dish made out of glass were checked.

0.3 Chapter overview

In the **first chapter** basics are explained, that means definitions, what PMMA and UV light are and what happens when PMMA is irradiated with UV light regarding chemical and physical changes. A literature research to the topic is made.

In **chapter 2** all materials and methods like atomic force microscopy (AFM), different kinds of roughness and force-distance curves are introduced. Also experiments are explained, which were divided into two parts. The first part observes changes in roughness directly after irradiation for different irradiation times and in the second part it is shown, how roughness changes when irradiated PMMA is stored.

Chapter 3 presents the results.

In **chapter 4** results are discussed and a conclusion is drawn, while **chapter 5** gives a short outlook for what results can be used for.

1 Basics

1.1 Definitions

1.1.1 PMMA

Polymethylmethacrylate (PMMA) is an organic substance, whose structural formula is shown in figure 1.

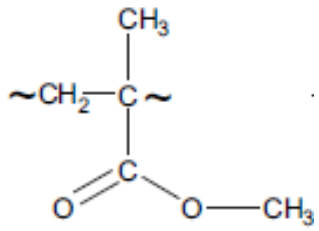

figure 1: Structural formula of PMMA

This material is a translucent thermoplastic, which is used in medicine for ophthalmic lenses, bone cement, dental prostheses, contact lenses, artificial eye lenses and other applications. In everyday language PMMA is known as Plexiglas®. Because this material is used also in other techniques very often, it is well known and because of applications in medicine also reactions to the human body were studied well and for a long time. [Trier2013]

1.1.2 Ultraviolet light

Ultraviolet light (UV light) is electromagnetic radiation with wavelength from 100 nm to 400 nm. UV light, which is invisible for the human eye, has a higher energy than visible light. [BfS2013] It is split into three regions, which are called UV-A (315 nm - 400 nm), UV-B (280 nm - 315 nm) and UV-C (100 nm - 280 nm). In the UV spectrum of the sun all of these regions can be found, but while UV-A and UV-B reach the surface of earth, UV-C is important for formation of the ozonosphere, but it does not reach surface of earth. [BLU2013]

Of course at high mountains atmosphere is not so thick, so the intensity of UV radiation is higher and also because of the ozone holes UV radiation became higher in the last recent decades.

UV light is also used in cosmetic purposes in solariums and to treat special skin diseases as well as in biological analysis for disinfection. For better effects UV light is used for entertainment in discos. Here of course UV light is produced artificial, while the sun light is a natural process. [BfS2013] For the keeping of some reptiles like turtles UV light is necessary, so UV applications are used in households without a professional advice.

1.2 Atomic force microscopy (AFM)

Atomic force microscopy (AFM), also called Scanning force microscopy (SFM), allows to image surfaces in the range of atoms. Contrary to scanning tunneling microscopy (STM) an observation of insulators is also possible. The detection is nondestructive. [Soe1998] [Kan2009]

1.2.1 Physical principle

For measurements small forces between atoms are detected, which can be smaller than intermolecular forces. These are forces of attraction, like van der Waals forces or ion bindings, and of repulsion, which are accrue because of Coulomb repulsion and Pauli forbiddance. While van der Waals forces decrease with increasing distance with a proportion $1/r^6$, repulsion forces decrease with a proportion $1/r^{12}$. So there is a point,

where modulus of forces is Null and another point of maximal attractivity which is situated at a bigger inter-atomic distance than the first point. Reach of these forces is less than 100 nm.

All these functions are imaged in figure 2.

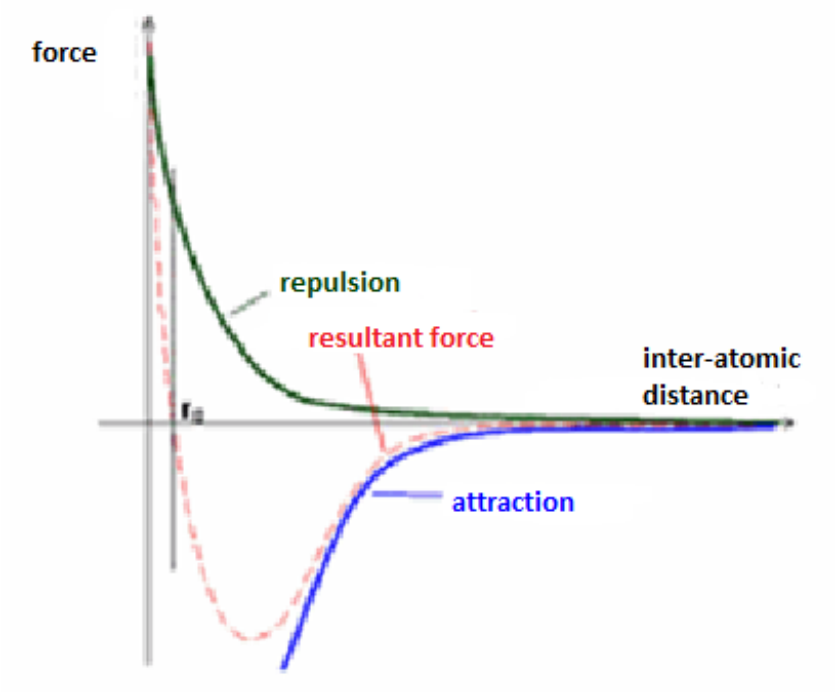

figure 2: Forces used at the AFM microscopy

The Lennard-Jones potential, that describes these forces is $U(z) = -4\,\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$. While ε is the minimal energy at the point of balance, σ is the distance, where modulus of forces is Null, so also is $U(z) = 0$. That is shown in figure 3. [Soe1998] [Kan2009]

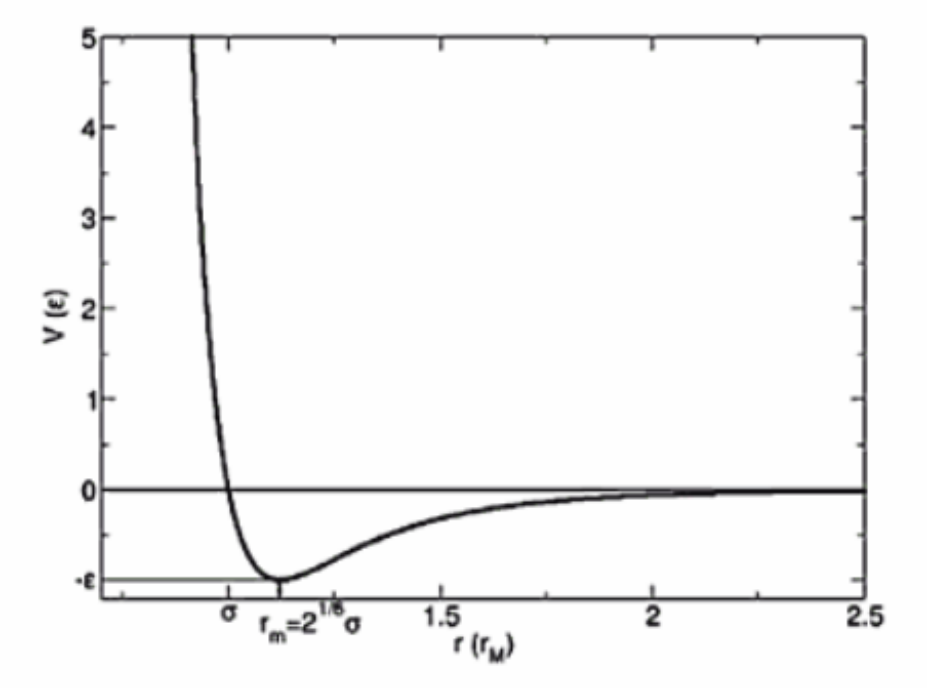

figure 3: Lennard-Jones potential. This is a sum of attractive and repulsive forces at a small distance to the atom

1.2.2 Construction

For detection of Lennard-Jones potential a very thin tip with a radius of 10 nm to 100 nm is brought on surface. This tip is fixed on an arm, which hangs on a spring. So the arm can move, what has to be detected. The oldest way to detect is, that tunnel current of the backside of the arm is used, which was measured by STM (scanning tunneling microscope).

Because this method is very complicated and expensive, two other methods were developed, which are shown in figure 4. There is an electrical way, where one electrode is on the backside of the arm and then the capacity is measured, on which the distance between two electrodes has an influence. Mechanical implementation is very expensive, so mostly the interferometrical way is used. Here a laser beam is split into one beam, which reflects on the backside of the arm and a reference beam, which is reflected on a mirror. When the arm changes position there is a path difference of both beams. Intensity of interfered beams is measured by a photodiode thus the distance can be calculated.

There are more methods, where instead of the laser beam an optical fiber is used, which is brought next to the arm. A reflex at the end of the fiber acts as a reference beam. There is also a possibility to bring a piezo layer on surface. Deflection means that renitency chances. [Soe1998] [Kan2009]

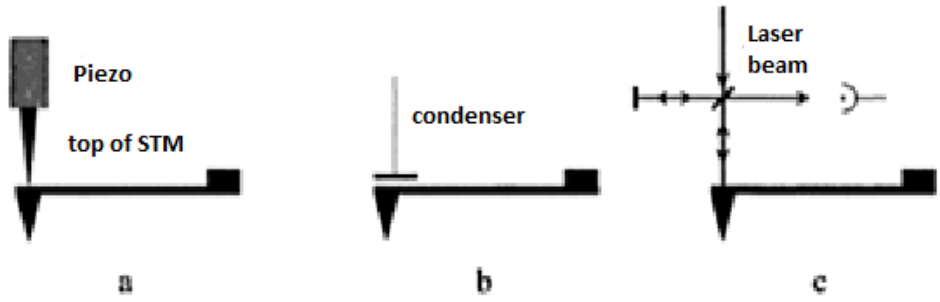

figure 4: Different kinds of detection: a.) tunnel-current-detection, b.) capacitive detection, c.) interferometric detection

1.2.3 Operating modes

There are different operating modes how to transfer the Lennard-Jones potential to the tip.

At the contact mode tip touches the surface and so system is in the front repulsive part of Lennard-Jones potential, which was shown in figure 5.

Here control signal is deflection of the arm. That mode is signalized by a big lateral and vertical resolution, but it has also a big noise, because there are friction forces between the tip and the surface.

By using non-contact mode the attraction region of Lennard-Jones potential is used. Arm swings with an amplitude of a few nanometers and a frequency of a few 10 kHz to 500 kHz. When the tip approximates surface, system gets an attenuation and the resonance is in smaller frequencies. Here control signal is frequency or amplitude. In this mode the tip does not touch the surface therefore this mode is absolutely non-destructive, more than contact mode. The downside is that the resolution is not as high as in the contact mode.

At the tapping mode the vibration amplitude is higher than in the non-contact mode. So tip swings into repulsing area of Lennard-Jones potential. Because of that there is a touch between the tip and the surface for a short time. Like in the non-contact mode amplitude is the control signal. High resolution is possible without a permanent contact with the surface like in the contact mode. There is a low-noise nondestructive map possible. [Soe1998] [Kan2009]

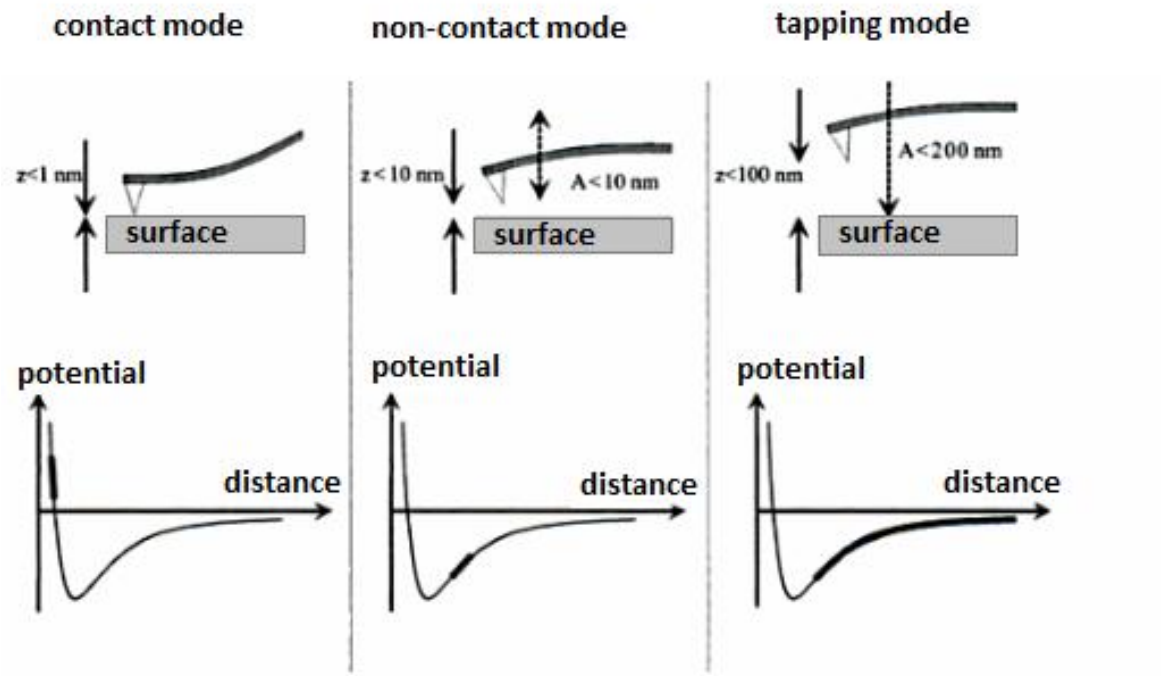

figure 5: Modes of AFM. At the upper picture it is shown, where tip is in different modes related to surface of sample. At the lower picture working point in Lennard-Jones potential is shown. While in contact mode distance is very low, tip is nearly touching surface, and so potential is very big, at non-contact mode distance is much bigger and potential causes attracting forces. At tapping mode distance changes much and potential in this area is very low.

1.3 Kinds of roughness

There are different kinds of roughness. Generally Roughness R is for two-dimensional profiles and S for tree-dimensional surfaces.

The distance between average height and the highest point is named Maximum peak high S_p and the distance between average height and the deepest point is Maximum valley depth S_v. That can also be seen in figure 6. Maximum height S_z is defined as

formula I: Maximum height

$$S_z = S_P + S_V$$

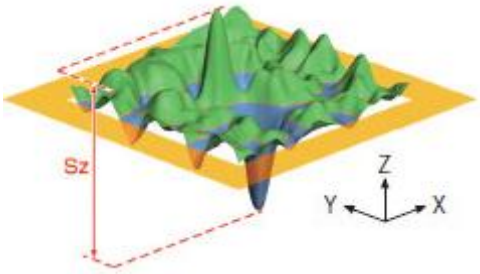

figure 6: Maximum height

These values only gives information about the highest and the deepest point, not about all the other points. For this roughness S_a was introduced, which is

formula II: roughness S_a

$$S_a = \frac{1}{A} \iint_A |Z\ (x, y)|\ dx\ dy$$

Roughness S_a is also shown in figure 7.

x and y are the directions on the surface Z. A is the area. S_a represents the arithmetic average of the deviations from the center plane. [SKC2007]

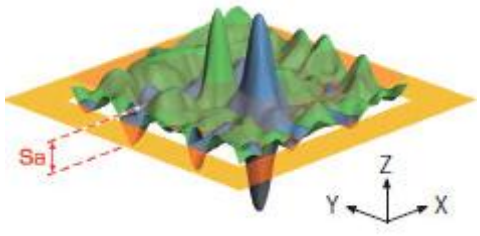

figure 7: Roughness S_a

There is also a second roughness that is shown in the figure 8 with

formula III: roughness Sq

$$S_q = \sqrt{\frac{1}{A}\iint_A |Z^2\,(x,y)|\,dx\,dy}$$

Roughness S_q includes the same information as S_a. [KaCh2008] [KaCh2009] [Oly2014]

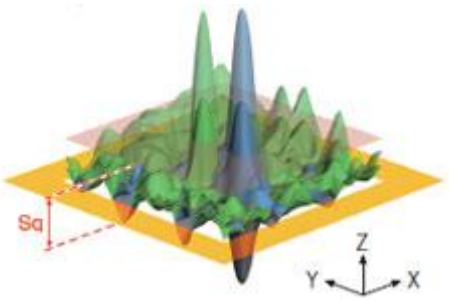

figure 8: Roughness Sq

1.4 Definition of the force-distance curve

In the modes of 1.2.3 forces are measured, but it is not measured how are they distributed in dependence of distance. This is done in force-distance curves.

AFM measures photodiode current I_{PSD} that is the result of the cantilever reflection and the position of piezoelectric translator. These two values have to be translated into force and distance with two more parameters, which are sensitivity and zero distance. For these two parameters there is no independent way to measure them.

Therefore a force curve is measured as a function of cantilever reflection as a function of sample position along z-axis (axis up and down). The relationship between force and cantilever deflection is

formula IV: Hooks Law

$$F = -k\,dc$$

Hooke´s Law. (F-force, k-spring constant, dc- cantilever deflection)

Force-distance curve is gathered. The linear part of this curve is assumed to be zero distance and its slope is sensitivity that is mostly correct or there is no significant problem. Such a curve can be seen in figure 9.

The tip has to make contact with the sample, but the point of contact is very difficult because of long-range forces and sample elasticity. For deformable materials with surface forces the point of first contact is a question of definition, because there is no significant point in the curve like in non-deformable materials or materials without surface forces. For extremely rough surfaces the point of first contact is also the zero point that can involve problems by tipping at an extremely high or deep point.

There are also differences between landing and lifting curve, because some forces, like adhesion vary in this case therefore both curves are always stated at the AFM. [NT2014] [BCK2005]

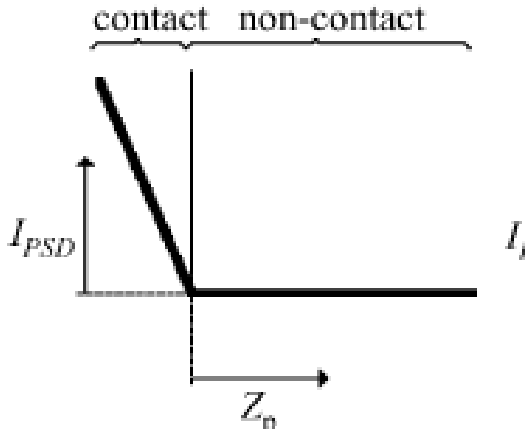

figure 9: Force-distance curve. The tip is landing, what shows the right horizontal line. The bend is the point where contact starts. The slant line on the left shows forces in material. For lifting that line is printed backwards.

1.5 Influence of the UV radiation

Irradiating a substance with UV light is always an entry of energy, what can bring molecules into other directions or organize them. It can also destroy chemical bonds or change the character of them. In the following sections the reaction is split into a chemical and a physical reaction.

1.5.1 Chemical reaction

As it was written in [WSM2004], UV light with a wavelength of 248 nm generates reactive sites. A plus and a minus pole are generated at the polymer and they accumulate to each other, because they are highly polarized. A cross linking between the ester side chain of two PMMA molecules arises, because of the Coulomb interaction. The incident UV photons activate the bonds electrically and introduce a chemical reaction between both ester sides. Therefore a methyl radical and a methanate radical are separated from the polymer. With this reaction the main chain of the polymer is broken and that becomes a new substance.

There is also another reaction at a wavelength of 193 nm explored in this article. In contrast to a wavelength of 248 nm there is no oxygen bridge between the ester sides, so between the methylene groups. There is also a second reaction at this wavelength. Here also a new chemical substance grows out.

After radiating with a wavelength of 308 nm no chemical reaction was observed.

In figure 10 chemical reactions are explained more exactly. [WSM2004]

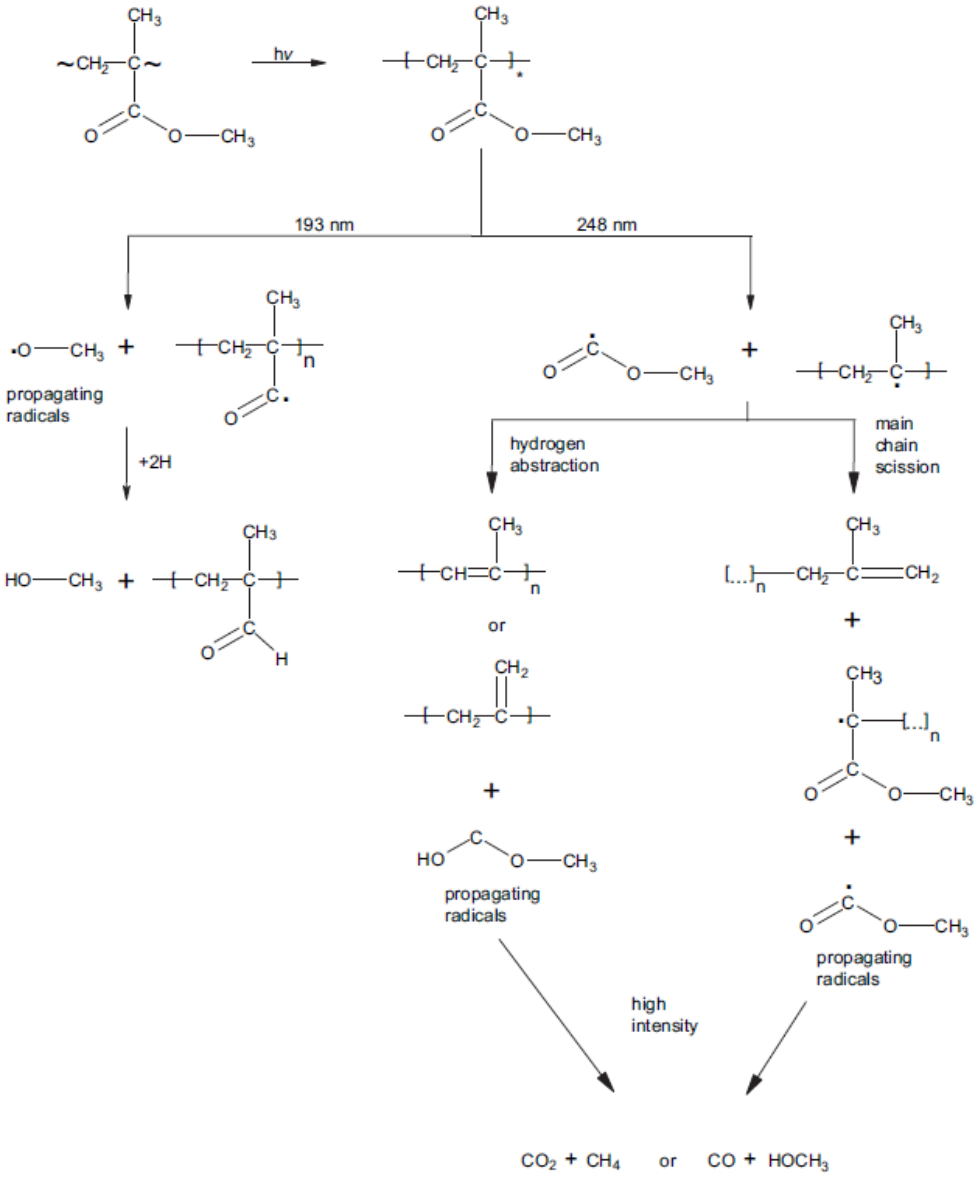

figure 10: Chemical reaction during irradiating PMMA with UV light. The wavelength were 306 nm, 248 nm and 193 nm. 306 nm was left out, because nothing changed in chemical structure.

1.5.2 Physical reaction

At irradiation of the UV light a photochemical reaction starts. Bonds are broken up because of entry of energy. Some scientific articles report how UV irradiation influences forces between atoms and how physical properties are changing.

1.5.2.1 Inner molecular bonds

In the article [ChJu2011] PMMA was irradiated by an electron beam and it was observed by Raman and X-ray photoelectron spectroscopy (XPS). Raman spectroscopy is a method to observe material characteristics by dispersion of light. So bonds and stretching become visible. With XPS chemical elements can be detected.

As it is shown in figure 11 there are peaks at C-O stretching, C-H bond, C=O stretching and C-H stretching at pure PMMA. Because all peaks disappear while irradiated, considerable amounts of hydrogen and oxygen atoms near the polymer surface are removed.

Instead of that two other peaks appeared, what means, that surface is transformed into hydrogenated amorphous carbon (a-C:H). With increasing electron fluency these peaks are growing.

Because graphic clusters are embedded into a-C:H structure hardness rises.

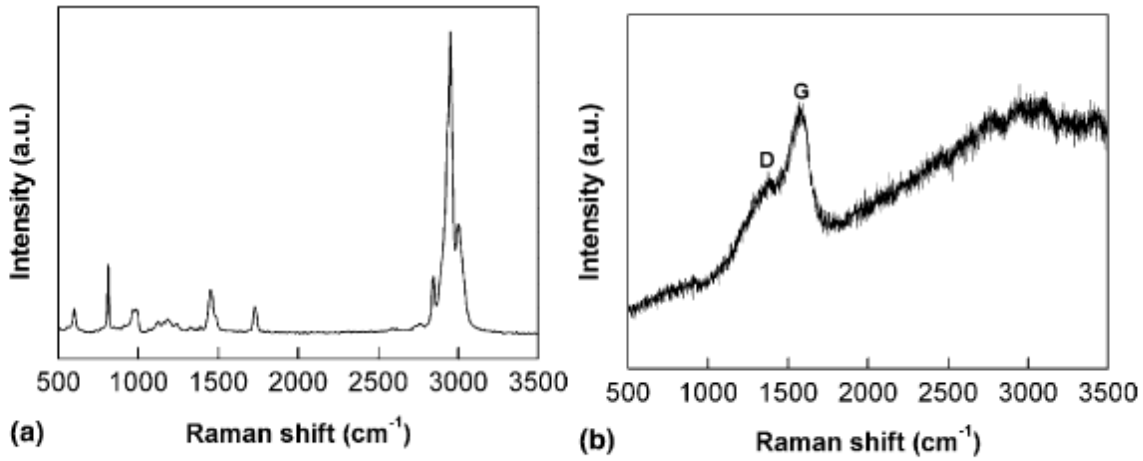

figure 11: Raman spectra of (a) pure and (b) irradiated PMMA.

Also observation with XPS shows a clear reduction of oxygen atoms. Polymer material is turned into carbonious material in depth of 50 µm. [ChJu2011]

In which way the behavior of an electron beam and UV light is the same is not clear and so these results cannot be used so easily.

1.5.2.2 Wettability

The reason for irradiation is that wettability rises. So for physical reaction it is very important to know what literature says about this behavior. When wettability rises contact angle becomes lower. Because it is much easier contact angle is measured in this experiment. How contact angle is defined it is shown in figure 12.

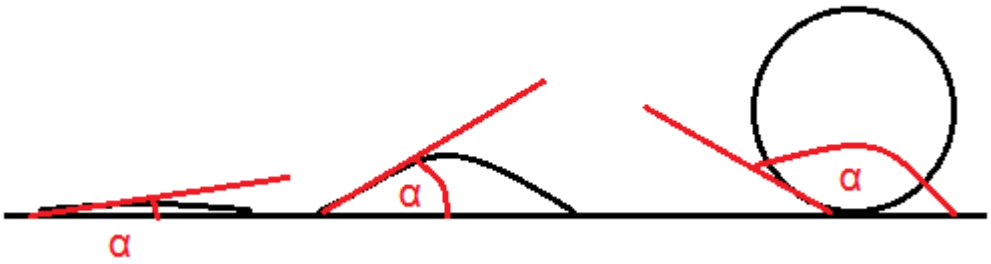

figure 12: Contact angle α. When contact angle rises, wettability becomes lower because the same volume of water has a lower contact area.

For the experiment in [DeLa2011] firstly PMMA was polymericied, that means heated up until bonds are breaking because of its thermal behavior. Than it was irradiated by an Hg-Xe-lamp (distance: 1.5 m, intensity: 3.5 W/cm², temperature: +200°C +-20°C, time: 0, 90, 210, 300 min).

For measuring wettability pictures of water drops at the surface of PMMA were made with an optical microscope and a camera. Then the angle was measured with the Photoshop software.

As it can be seen in figure 13 contact angle (α) and so wettability, rises and reaches a maximum at the irradiation time of 150 min. After that time hydrophilic properties change into hydrophobic ones again.

The reason is that wettability is affected by electrical charging of the surface, what is influenced by UV irradiation. A hydrophilic behavior means negative charges. [DeLa2011]

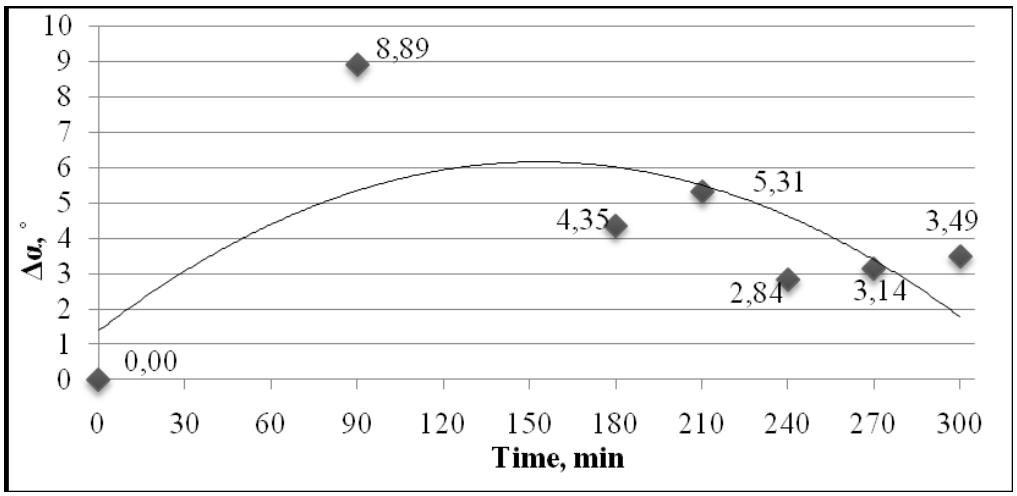

figure 13: Increment of Contact angle as a function of irradiation time

In the bachelor thesis [Tru2013] contact angle was observed at the same conditions after irradiation and then storage for some days in different materials. For storage in air there was a rise of contact angle for 5 min, 45 min and 120 min irradiation time, what can be seen in figure 14. [Tru2013]

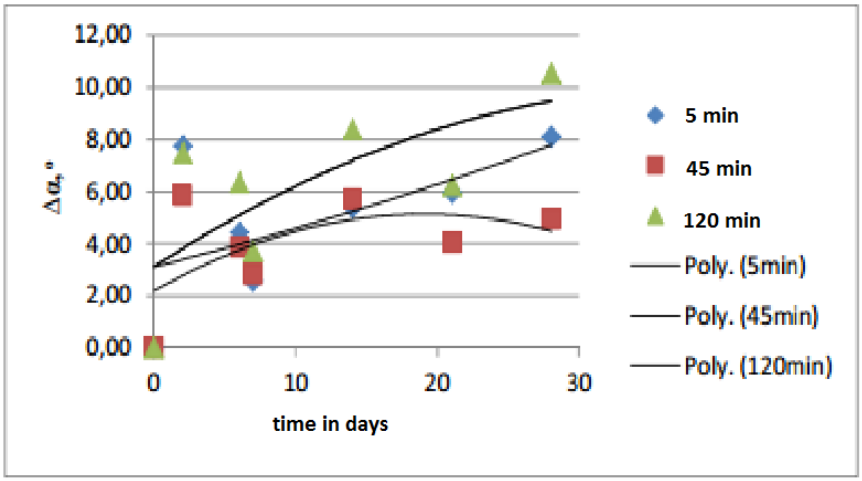

figure 14: Increment of contact angle as a measure for wettability in dependence of storage time after irradiation for different irradiation times. Storage time is in days and it happened in air.

figure 15 shows, that in the first 8 days of storage something happens in the material and contact angle changes very fast for an irradiation time of 45 min. After these 8 days contact angle stays constant, but at different values. So PMMA, which was stored in glass, had the biggest contact angle, while in paper stored PMMA had the lowest one.

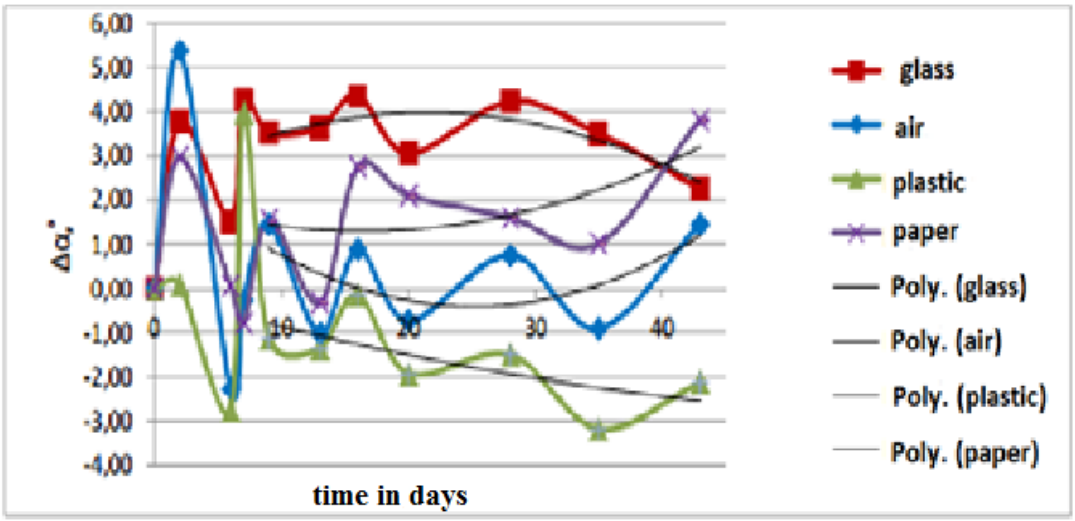

figure 15: Increment of contact angle as a measure for wettability in dependence of storage time (in days). Storage happened in glass, air, plastic and paper. The Irradiation time was 45 min.

For an irradiation time of 5 min also PMMA stored in paper and in glass had the biggest contact angle, but in this case PMMA stored in paper had a bigger contact angle than storage in glass. Storage in plastic and air brought lower contact angles, what is shown in figure 16. Contact angles stood constant in the time of 10 to 60 days. The first 8 days, which are interesting because contact angle changes, were not observed in this experiment for 5 min. [Tru2013]

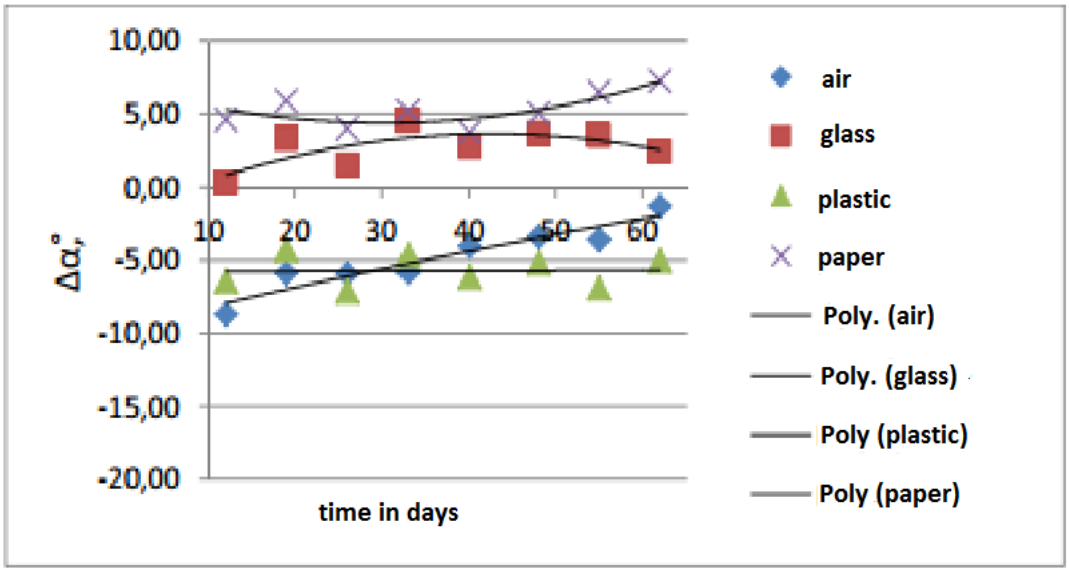

figure 16: The same diagram like figure 14. Here irradiation time was 5 min.

For 120 min the same order of contact angles like for 45 min were observed as can be seen in figure 17. [Tru2013]

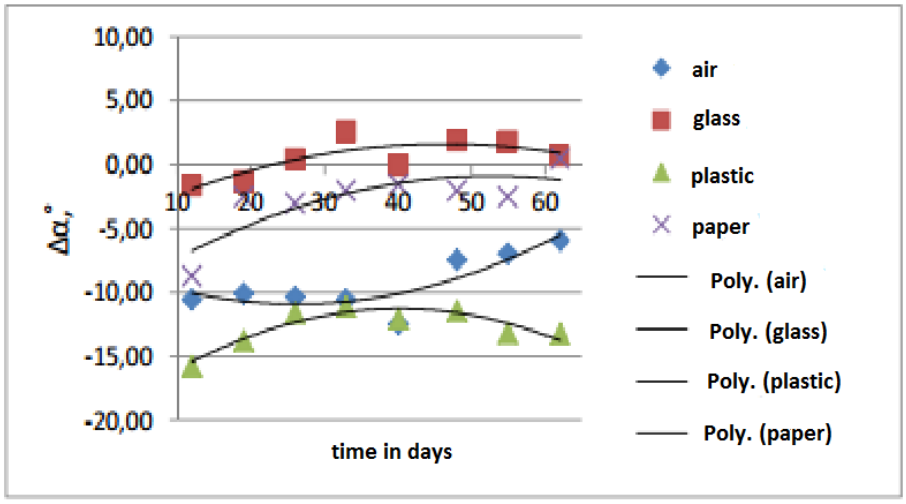

figure 17: The same diagram like figure 14. Here irradiation time was 120 min.

There was a second group of PMMA samples, which were bought together with the first group and also stored together with them. Because of an unknown reason contact angle of this group reacted differently. So just after 30 days contact angle stood constant for all irradiation times. Also here was no influence for an irradiation time of 5 min like in the first group, what is imaged in figure 18. [Tru2013]

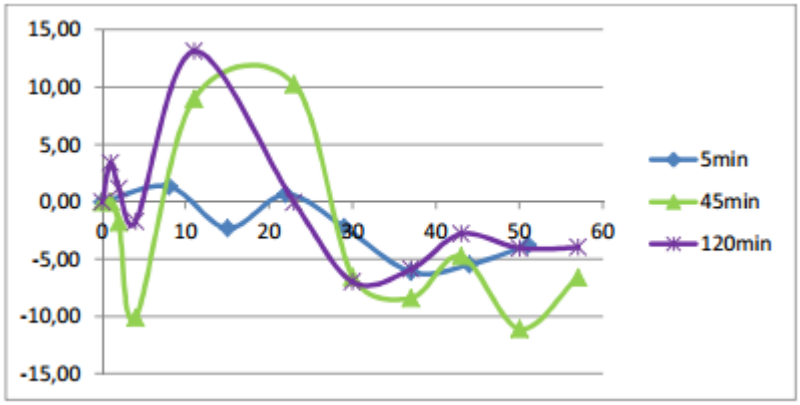

figure 18: The same diagram like figure 14 for a second group of samples, which had the same conditions like the first group but another behavior because of an unknown reason.

Also for storage in different materials this group differed from the first group. So paper and glass did not have the biggest contact angles like in the first group. All that can be seen in figure 19. [Tru2013]

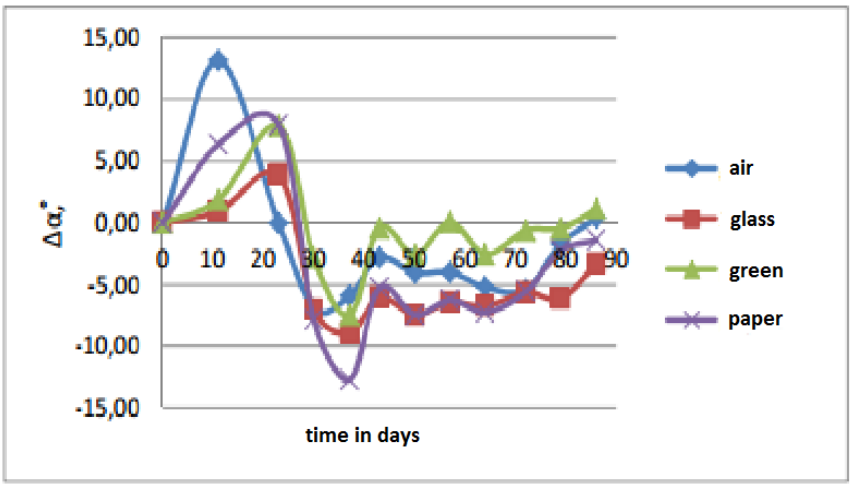

figure 19: Different storage conditions like in figure 15 for the second group. The irradiation time was 45 min.

In [TWL2012] a 2 mm thick plate of PMMA was moistened with an ethanolic solution (90 % Ethyl alcohol and water) and over this a second plate was lawn. After that it was irradiated by 234 nm UV light for less than 1 min with an intensity of 225 mW/cm².

After irradiation both plates were detached washed by distillated water, dried and then contact angle was measured. The results can be seen in figure 20. [TWL2012]

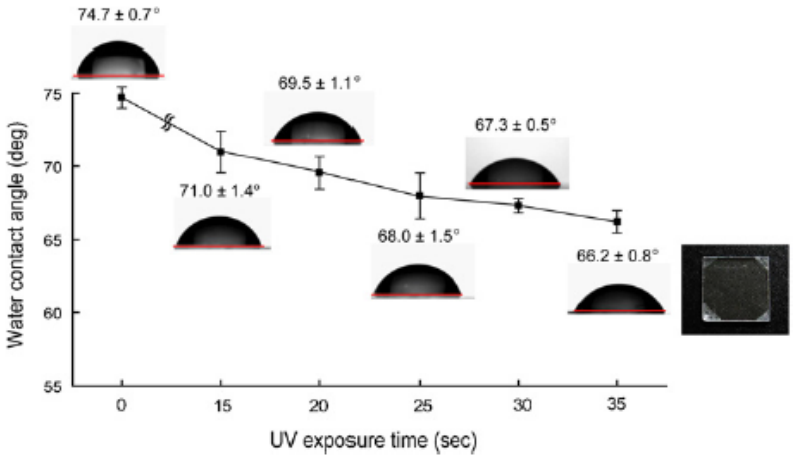

figure 20: Contact angle after irradiation according to the article [TWL2012]. Between two plates PMMA 90 % ethanol was used and then it was irradiated.

With increasing irradiation time contact angle decreases in the first 35 seconds of irradiation. Maybe the reason is, so the article says, surface carbonyl groups were destroyed by solvent dissolution and UV irradiation when there is a strong interaction between the ester carbonyl group of PMMA and the hydroxyl group of ethanol with a high energy input. [MRS2007] [TWL2012]

In the first hour contact angle changes very abrupt, but in the first 15 min changing was negligible. So bonding has to be realized in the first 15 min after irradiation. After 3-4 h effect of irradiation has completely disappeared, as is shown in figure 21.

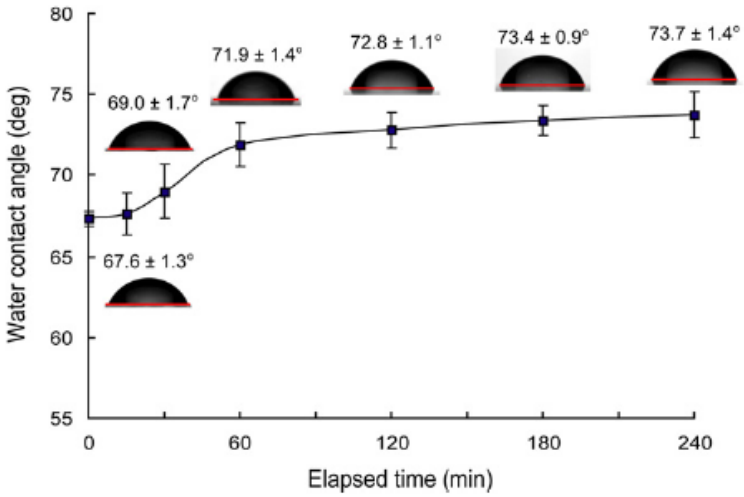

figure 21: Contact angle measured after 30 s irradiation time and an elapsed time.

During this experiment it could be easily seen, when bonding started, because than PMMA started to become murky because of Newton rings. When bonding finished, PMMA looked like before irradiation. In this experiment until 15 s irradiation time there was no change and after 20 s regions became murky and so surface started to change. After 25 s it seemed that bonding between the two plates started, and after 30 s murkiness disappeared and bonding finished.

Plates were fixed with this experiment by irradiating 30 s. Strength rises with a bigger solution until 70% and then it stayed constant. Under 50% bonding was reversible, when higher solutions were used bonding was permanent. [TWL2012]

1.5.2.3 Absorbance

In the article [DeLa2011] also absorption was observed. The results are shown in the figure 22. Because PMMA is used for contact lenses it is very important, that material is translucent. So absorbance has to be low. The other point is, that PMMA is irradiated and so just light can operate, which is absorbed, but in this case it is UV light, which has a different absorbance.

Absorption is almost zero for the region of 340 to 370 nm and in the region of 370 to 400 nm it rises and falls again, so there is a higher absorption. [DeLa2011]

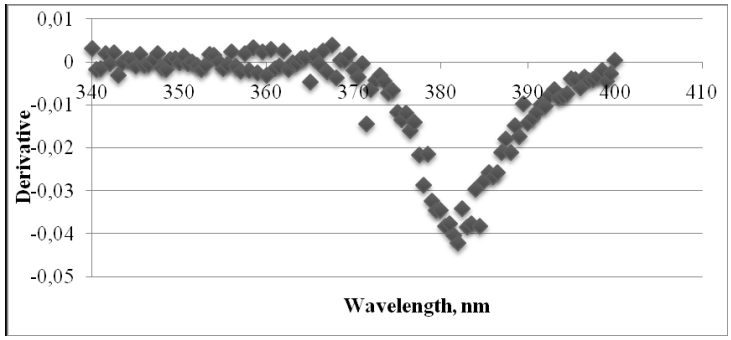

figure 22: Absorption of PMMA. Here absorption spectra is demonstrated. So at the minimum at 380 nm absorption is high.

For wavelength of 200 to 340 nm the article [CTH2008] reports about absorbance. There is a big maximum at 216 nm, what can be seen in figure 23. [CTH2008]

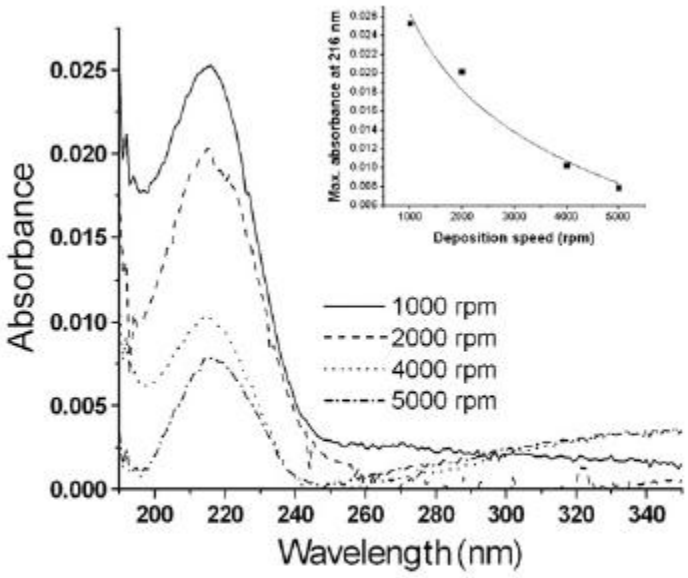

figure 23: Absorbance of PMMA films for UV spectra with different spin speeds (for putting PMMA on substrate). The maximum of absorbance was at 216 nm.

In the article [YTT2005], where figure 24 is found, it was said, that the maximum at 220 nm comes from the unsaturated C=C bonding in PMMA. All conditions of this experiment are explained in 1.5.3.4. [YTT2005].

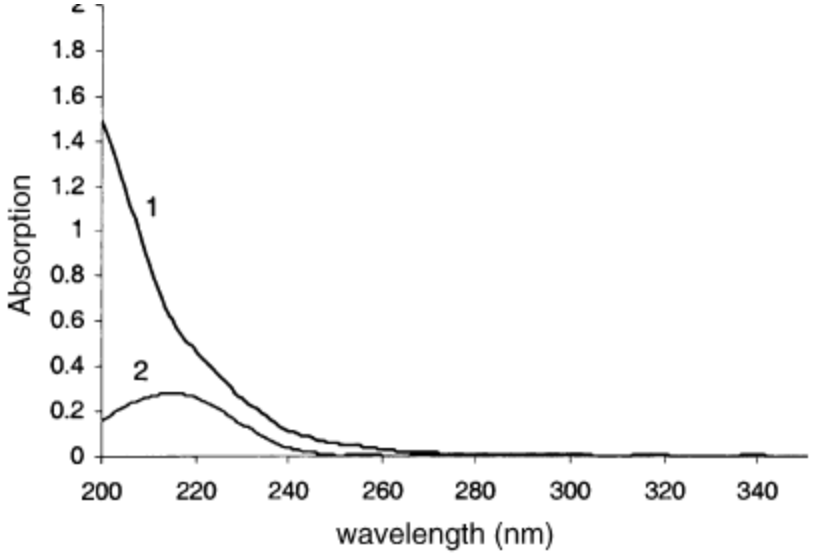

figure 24: UV spectra. (1) shows spectra after 1 min irradiation and (2) is pure PMMA.

1.5.2.4 Hardness

When hardness changes something like density or chemical bonds are changing and because surface is a part of material there is a correlation between hardness and surface topography. So it is good to look also at hardness.

The second point is, that this experiment happened in the same conditions like the following experiments of surface topography. So this results can be used without problems.

Hardness falls in the first 5 min and after 45 min up to 120 min it rises again to start value at irradiation with an intensity of 3500 mW/cm² (200 to 400 nm, maximum at 365 nm, distance: 40 cm) in air, what was reported in [Sche2013].

Low wavelength, so in this experiment 220 nm, had a big influence to hardness while high wavelength had lower influences and at 380 nm there was no visible influence anymore. So irradiation with the biggest absorbance, what is explained in 1.5.2.3 had also the biggest influence to hardness.

Conditions while irradiation also had an influence, so hardness fall slower in vacuum than in air in the first minutes. [Sche2013].

1.5.3 Literature research for surface topography

1.5.3.1 Roughness changes for PMMA on iron substrate

In the article [DSSM2010] PMMA was brought on iron substrate and it was irradiated by a mercury lamb (UV-C light: 200-280 nm, 3.6 W/m², distance: 1 m). Surface was observed by AFM in contact mode in three regions on each sample with the size of 25x25 µm² and 50x50 µm using a scan frequency of 0.8 Hz.

The result is, that roughness S_a is rising while looking after 0, 90, 500 and 920 h after every step of irradiation. So it rises from 83.2 nm for non-irradiated PMMA to 272.4 nm after 920 h irradiation time for a scanning area of 25x25 µm² and from 286.9 nm to 484.4 nm for 50x50 µm² size. Out of these results it is also good to observe, that there is a higher roughness S_a for a bigger scanning area.

PMMA has got a flat surface with some small bumps on it. Surface roughness increased moderately after 90 h irradiation time. After 500 h irradiation time there was the same

surface morphology with the same roughness and after 920 h roughness fell. But after 500 h hills, voids and micro cracks appeared, which become bigger and deeper after 920 min. [DSSM2010]
AFM pictures are shown in figure 25.

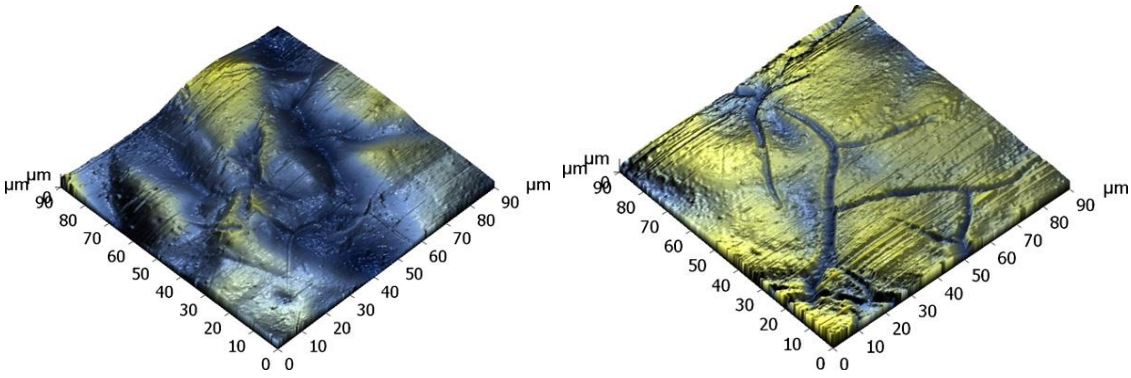

figure 25: Surface of PMMA after an irradiation time of 500 and 920 h. The pictures were made with AFM and the scanning size was 90x90 µm².

1.5.3.2 Roughness changes for 18 month irradiated PMMA

An irradiation time up to 18 months had the specimen in the article [MCJ2012] in a humid atmosphere. A xenon arc lamp was used with a wavelength of 300 nm to 400 nm and an intensity of 114W/m^{-2}. Special filters limited wavelength. Specimen were placed on a carrousel, that rotates around the lamp. In this article PMMA was separated into hazy and yellow after its optical behavior. There were difference because manufacturer was not the same. Surface morphology was studied by AFM (semi-contact mode, scanning sizes: 90x90 µm² and 20x20 µm²) and SEM (scanning electron microscope).

The result was that roughness increased, particularly for stressed specimen while irradiated. There were cracks with a crack length in the order of hundreds of micrometers and also pores in this range. Hazy specimen were rougher in all, but behavior while irradiated was similar to the yellow one.

In figure 26 results are shown. It is clearly visible in SEM pictures, that micro cracks and holes appeared and that roughness rises can also be seen without measuring. Roughness S_a rises for hazy specimen from 3.1 nm to 26.0 nm after 12 months and for yellow from 2.6 to 21.9 nm. The scanning area was 20x20 µm². [MCJ2012]

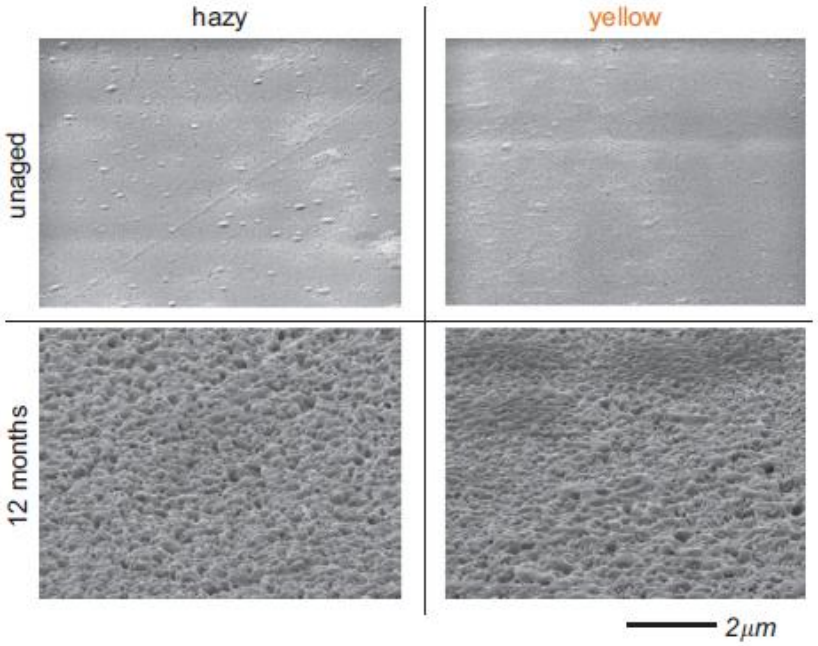

figure 26: SEM pictures of surface of PMMA. Hazy and yellow specimen are splitted after their optical behavior. The upper pictures are from pure PMMA (unaged), in the lower pictures PMMA was stressed with irradiation for 12 months.

1.5.3.3 Roughness changes for PMMA on aluminum and glass substrates

In the article [ACC1996] PMMA films on aluminum and glass were irradiated by a mercury lamb with a wavelength of 254 nm in air (intensity: 2.11 mW/cm², distance: 4 cm). For roughness analysis AFM in contact mode was used.

Roughness of these thin films depended on substrate, so roughness of PMMA of glass was lower than when substrate was aluminum also before irradiation because of preparation technology. The reason is, that there is a relatively strong base-acid interaction, that influences the film morphology for a film on glass during preparation. [ACC1996]

After 120 h irradiation time roughness was higher than before irradiation, but in the case of aluminum substrate irradiation was more effective so roughness became much higher than in the case of glass substrate, but it also was more rough before irradiation.

In the case of glass roughness rises during the irradiation because of a big number of voids, which are randomly distributed on surface. It is reported, that the development of the surface during irradiation has a strong influence on further oxidative degradation. So the access of oxygen, free radicals and so on to the polymer is facilitated and more active points are available. Because of the chemical reactions material becomes less homogeneous and roughness rises.

Between PMMA and aluminum there is just a low adhesion. Because of its amphoteric character interactions with PMMA are characterized by weak base and properties are rather negligible. [ACC1996]

In the article [KaCh2008], where the same experiment was done (intensity: 3.2 mW/cm², distance: 10 cm) the same was observed. Here solvents were used as well and solvent depends on roughness before and after irradiation. While chloroform and chlorobenzene cause a rise of roughness for glass and aluminum substrate, toluene causes a fall for glass substrate and a rise for aluminum substrate. When using acetone and terahydrofuran roughness falls for both substrates.

The reason is that different solvents influence chemical reaction during irradiation differently. [KaCh2008]

1.5.3.4 Thin films irradiated for 4 min with UV light

In the article [YTT2005] thin films of PMMA on silicon substrate were irradiated by a mercury lamp with a spectrum of 250 to 460 nm, a distance of 17 cm and an intensity of 70 mW/cm². There was no change of roughness after an irradiation time of 4 min, but there was a thickness reduction up to 22.9 % for a thickness of 1.1 µm. For thicker films reduction was less. In the case of 5.2 µm it was just 9.9 %. Refractive index increases and there was a mass loss of 14 %, so the article comes to the result that there has to be a chemical change in the material. [YTT2005]

It was also said that shorter wavelengths have bigger influence than longer wavelengths especially to the refractive index. The same was observed in [Sche2013] in 1.5.2.4.

In this article FT-IR spectrum (Fourier transform infrared spectroscopy) was also observed, as is shown in figure 27. Out of the refractive index it was said that a maximum at 220 nm comes from the unsaturated C=C bond. There were some more effects as well such as a reduction of C=O stretching band at 1730 cm^{-1} after irradiation and also at C-O stretching band double peak, which was at 1150 cm^{-1} and 1180 cm^{-1} before irradiation and at 1240 cm^{-1} and 1268 cm^{-1} after irradiation. A weak absorption at C=C peak at 1630 cm^{-1} and at -OH at 3500 cm^{-1} appeared. [YTT2005]

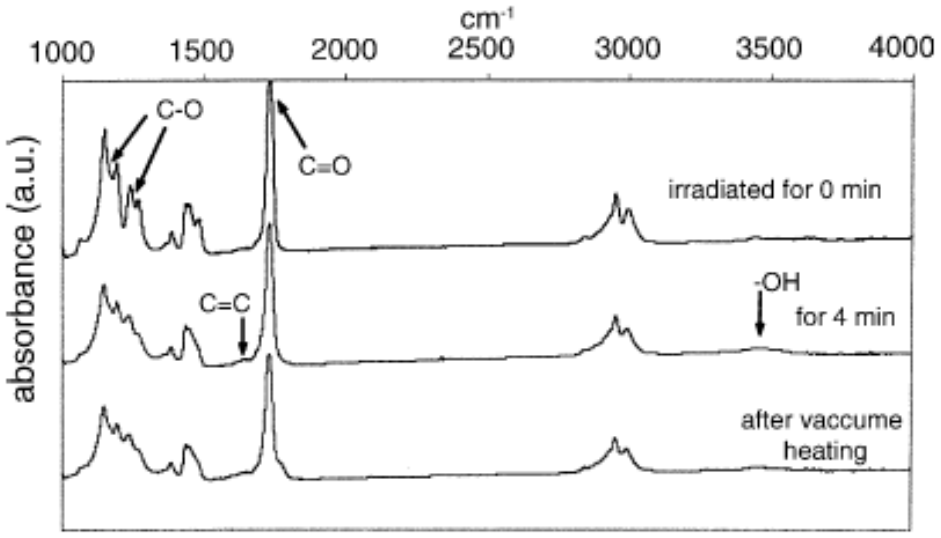

figure 27: FT-IR spectrum of pure PMMA, 4 min irradiated PMMA and PMMA after heating in vacuum at 100°C for 4 h (last one is not within the topic therefore is not explained).

From the given information a degradation scheme can be created, as is shown in figure 28.

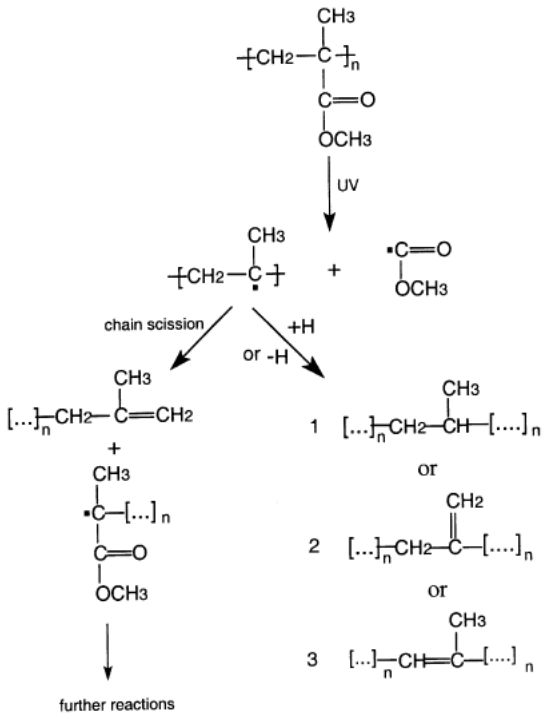

figure 28: Simplified degradation scheme of irradiated PMMA after [YTT2005].

Carbon radicals are formed by irradiation, which are not stable, so there have to be more reactions of the main chain scission and the formation of saturated or unsaturated aliphatic structures. They have to capture or eliminate the hydrogen radical.

There has to be a theoretical mass loss of 59%, but 20.6 % were reached at most. So it is assumed, that not all molecules are involved in this reaction. [YTT2005]

It is not clear, in which way substrate or the fact, that these are thin films influences results, but because of the low time of irradiation this article was introduced here.

1.5.3.5 Irradiation of thin films with a 157 nm laser

In the article [SKC2007] a thin film of PMMA on a film of SiO_2 on silicon substrate was investigated by irradiation with 157 nm light of a laser for 3 min (fluency: 13.5 J/cm²).

Average roughness rose significantly, because some peaks in the form of islands grow out. Surface between these islands had the same roughness as before. If irradiated for a longer time more islands appeared, while both the islands and the roughness between islands were changing.

Histograms of height of PMMA were made. For the non-irradiated case roughness histogram was symmetric and also for irradiation time of 1 min. After 3 min time surface roughness histogram consisted of two distinct island size distributions at 38 and 70 nm (scanned area: 30x30 µm²). Surface roughness shifted towards larger structures. Histograms are shown in figure 29.

In the article roughness S_q was measured and also maximum height, deepest valley and peak to peak value. All of these values are rising with an increasing irradiation time.

In the case of 157 nm irradiation all changes are ablated through the photo chemical dissociation, because the heat entry is very small and this effect is much bigger with larger wavelength. [SKC2007]

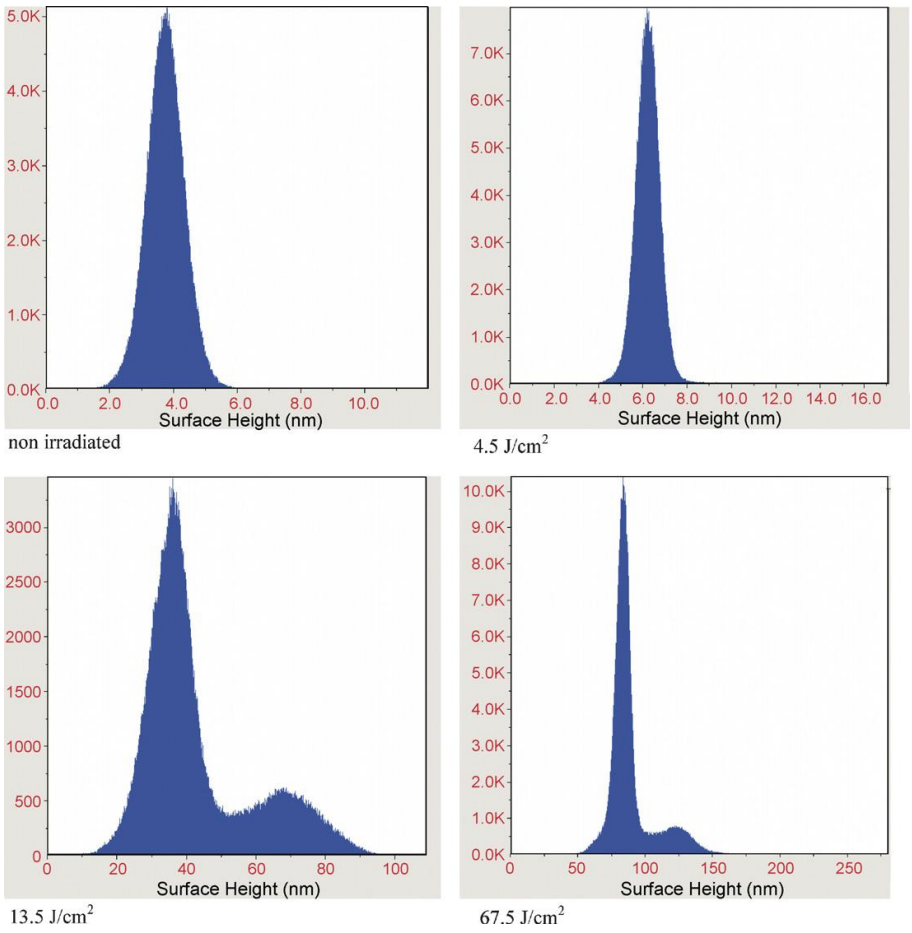

figure 29: Height distribution histogram of PMMA irradiated with a 157 nm laser with a scan size of 30x30 µm².

2 Materials and methods

2.1.1 Preparation of samples

Commercial PMMA was used for the experiments. To protect PMMA against scratches foil was placed on the surface of PMMA. For using it in experiments the foil was removed and then samples were brought into an ultra sound bath for 5 min. Samples were dried with commercial cellulose and after that the rest of dust was blown off with compressed air.

Four regions were marked for taking pictures in this area. To see if the size of the picture has an influence on measured roughness, firstly a region of 50x50 µm² was scanned and after that a region of 20x20 µm². The centers of both squares were the same.

2.1.2 Used AFM and tip

For all of these experiments an atomic force microscope of the Russian company nt-mdt company was used.

For measurements the tip NSG01 from the company NT-MDT was used. (Chip size: 3.4x1.6x03 mm, Reflective side: Au, tip height: 14-16 µm, tip curature radius 10 nm, Aspect ratio: 3:1-5:1; Cantilever length: 125±5 µm, Cantilever width 30±5 µm, Cantilever thickness 1.5-2.5 µm, Resonant frequency 87-230 kHz, Force constant, 1.45-15.1 N/m)

2.1.3 Irradiation times

2.1.3.1 Measurement automatically with AFM software

To find out, if roughness is changing, PMMA was irradiated with an UV lamp (intensity at 0 cm distance: 3500 mW/cm², distance: 40 cm) for different times. Before and after the irradiation four pictures in the marked areas were made with an AFM with 50x50 µm² and 20x20 µm² size in tapping mode.

For editing, firstly a good part of the picture without dust was chosen and it was cut out with the function "Cropping". Pictures were made flat with fit lines (Polynomial order: 2) in x and y direction then, because samples laid slant in AFM by taking pictures. After that roughness S_a was measured with the software.

AFM pictures are shown in the figure 30.

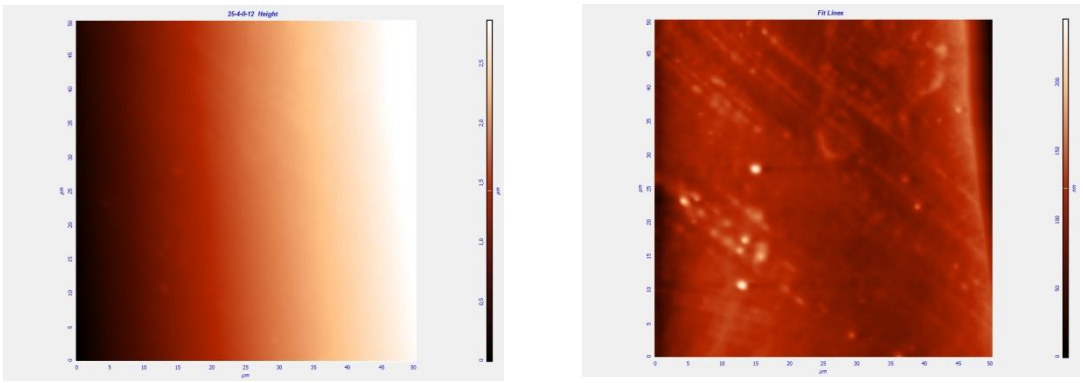

figure 30: AFM picture before and after function fit lines

The number of pictures made is shown in the table 1.

table 1: Number of pictures for different irradiation time. 4 pictures were taken of every sample. Sometimes pictures could not be used.

Irradiation time in min	0	5	15	30	45	60	75	90	105	120	135	150	165	180	195	210	240
50 µm	48	16	16	18	26	18	11	10	23	13	8	4	11	6	4	8	4
20 µm	50	15	14	20	24	20	10	11	22	15	8	4	11	7	4	7	4

Software, which was used to operate the AFM had the possibility to calculate roughness automatically. Name and version of the software used was Nova 1.0.26 RC1 that was sold in 2004 by NT-MDT.

For the case of a Gauss-distribution standard distribution is σ, X is Roughness for one picture and $\overline{X}$ the average of all measurements while n is the number of all measurements.

formula V: Standard deviation

$$\sigma = \sqrt{\frac{\sum(X - \bar{X})^2}{n - 1}}$$

This formula is valid for many measurements. For a small number of measurements it is necessary to use t-distribution. Both distributions are shown in figure 31.

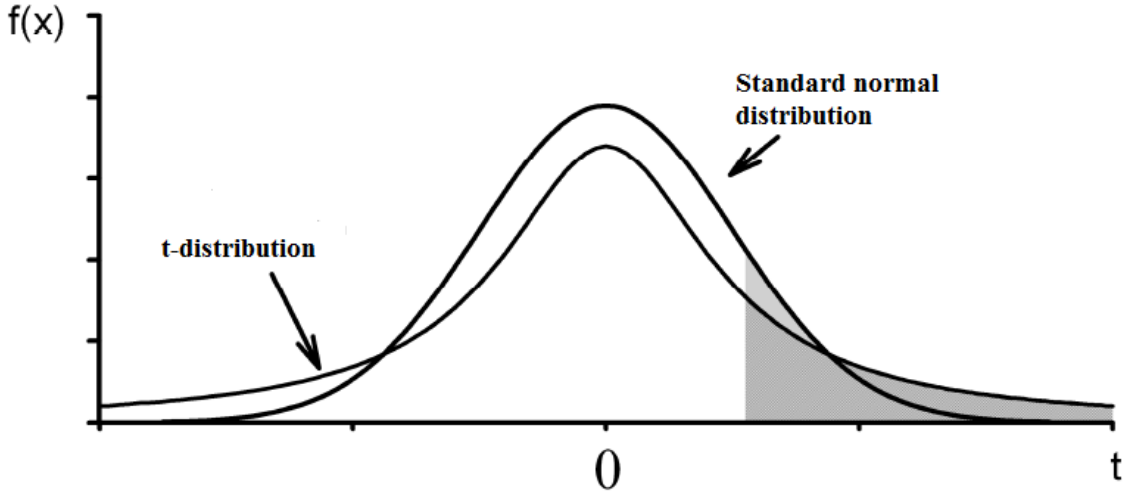

figure 31: Difference between t-distribution and standard normal distribution

formula VI shows distribution with correction factor. This factor is depended of the number of measurements and of one-sided t-distribution factor.

formula VI: Variation of roughness S_a

$$\Delta S_a = \frac{t}{n-1} \cdot \sigma$$

n is the number of measurements and t, one-sided student factor, is a value of t-distribution, which is published in tables for mathematics. [RF2014]

2.1.3.2 Measurement with histograms

For having a second option to see what is happening at irradiation of the 50x50 µm² pictures at 2.1.3.1 height profiles of some lines of the picture were taken out after making the picture flat with fit lines. All dust, what was in the picture was cut out. Height profile is also made automatically with the AFM software.

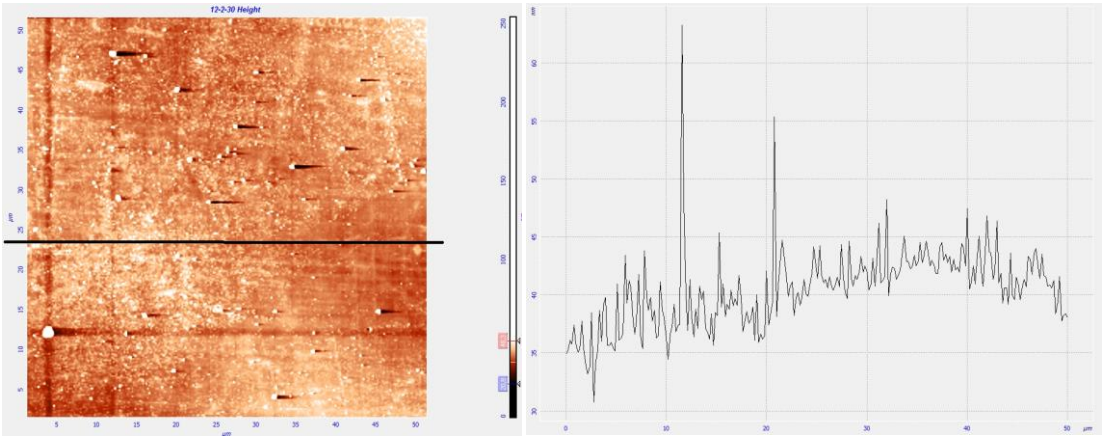

figure 32: Height profile

Out of the three profiles of each picture histograms were made of height for each point in this line. For having good histograms from every value the average of the whole line was subtracted.

For comparing these histograms it couldn´t be assumed, that the histograms are Gauss distributions. So a mathematical expectation M was calculated, which describes area under histogram curve.

formula VII: Mathematical expectation of the histograms.

$$M(x) = \sum min_{bin} \frac{n_{bin}}{n_{all}}$$

In this formula $\mathrm{min_{bin}}$ is the smaller border of one bin, $\mathrm{n_{bin}}$ says, how many values are in this bin and $\mathrm{n_{all}}$ is the number of all measurements in the hole histogram. Of course M depends on measured height values x.

Dispersion D is a value for the width of histogram.

formula VIII: Dispersion of histograms.

$$D(x) = M(x^2) - [M(x)]^2$$

$\frac{M}{D}$ is a measure for roughness, which is read out of histograms. When this value is small, also roughness is small and when it is bigger also roughness is bigger. Because only the changes are necessary and not an absolute value, there does not have to be a relation to the roughness Sa. Unit of $\frac{M}{D}$ is nm in this case.

For the quality of measurements the following calculations were made:

formula IX: Distribution for M/D

$$\Delta \frac{M}{D} = \left(\frac{\Delta D}{D} + \frac{\Delta M}{M}\right) \cdot \frac{M}{D}$$

formula X: ∆M

$$\Delta M = \sqrt{D}$$

because of the definition of dispersion.

formula XI: ∆D

$$\Delta \boldsymbol{D} = \boldsymbol{D_{max}} - \boldsymbol{D_{min}}$$

with $D_{min} = D \cdot \gamma_1^2$ and $D_{max} = D \cdot \gamma_2^2$

γ_1^2 and γ_2^2 are student factors out of two-sided t-distribution, which can be read out of mathematical paper. For this experiment a plausibility of 90% is assumed thus $\gamma_1^2 = 0.795$ and $\gamma_2^2 = 1.3$. [RF2014]

In the next step all values were put in formula IX and brackets were solved, so formula is

$$\Delta \frac{M}{D} = (\gamma_1^2 - \gamma_2^2) \cdot \frac{M}{D} + \frac{1}{\sqrt{D}}$$

So the formula with all the values is

formula XII: Error M/D with values

$$\Delta \frac{M}{D} = 0.505 \cdot \frac{M}{D} + \frac{1}{\sqrt{D}}$$

2.1.3.3 Measurement with force-distance curve

As a third option force-distance curves of the tip were made at the same time like the pictures and always after scanning the picture in the middle of the picture. Therefore the contact mode was used.

For this option a force-distance curve is measured, which has a blue color in the figure 33 and also a curve, when the tip comes back, which is red here.

For calculating with these graphs the angle, which is marked in figure 33, has to be measured. This angle is the relationship between force and distance. For a very smooth surface suddenly maximum of forces is on the tip while approximating. At a rough surface force grows slowly while approximating. [RF2014]

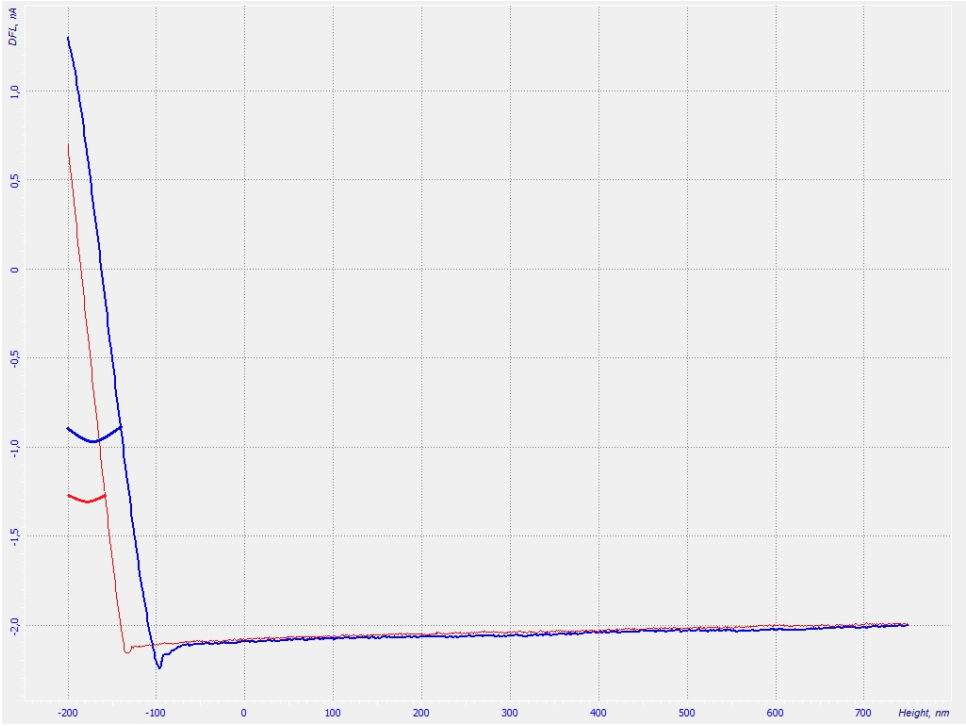

figure 33: Force-distance curve for landing (blue) and lifting (red). Tip approximates from the right side of picture to the left side, where is the sample and goes back again. The marked angles were measured and used for calculating.

A big angle α means a smaller roughness, because for a very flat surface all atoms are in one plane and so also forces reach to one definite height. When tip approximates all forces begin to appear suddenly at the same time. Angle α is nearly 90°. At a rough surface there are hills and valleys, so some atoms are higher than others. So at approximating forces of one atom appears and later the force of another one. Force becomes higher by approximating. Angle α is smaller.

For the plausibility check the following formula was used, which is analog to formula VI:

formula XIII: Variation of angle α of force-distance curve.

$$\Delta\alpha = \frac{\sigma}{N-1} \cdot t$$

2.1.4 Storage

In this experiment each 3 samples were irradiated for 75 min and for 180 min and stored in the air or in a closed Petri dish out of glass. Two strikingly irradiation times out of the results of the experiment were taken.

For comparison also each 3 non-irradiated samples were put to the irradiated samples. After the definite time samples were scanned with the AFM like in the 2.1.3 and all measurements were done as shown 2.1.3.1, 2.1.3.2 and 2.1.3.3 and also calculation was done the same way. In the first two weeks every second day roughness was measured and later once a week until day 54.

Of course it is possible, that room conditions are changing, so humidity and temperature also has to be measured.

3 Results

3.1 Irradiation times

3.1.1 Measurement with AFM software

The AFM pictures of non irradiated PMMA were completely flat, but after the irradiation some holes or sometimes hills were observed, like it is shown in figure 34. The problem is that there were also flat surfaces at another place of the same sample and at longer irradiation times holes and hills disappeared. So it was impossible to find a point where it appears or disappears. Sometimes even after 5 min these effects were seen and in other cases after a very long irradiation time not.

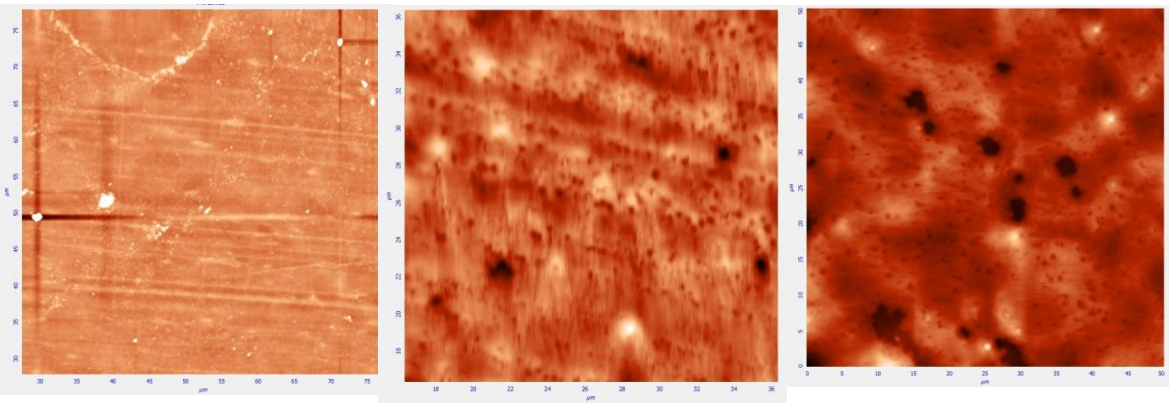

figure 34: AFM pictures after processing with fit lines. Irradiation times were 0 min, 90 min and 105 min. Holes are observed after irradiation, but sometimes they did not appear at other places at the same sample.

Measurement with roughness analysis from the AFM software Nova brought the result, which is presented in figure 34. To see, if there is an influence of the size of the picture, sizes were split into two graphs.

In general roughness does not rise, but there are two peaks in the graph where roughness rises and by irradiating for a longer time roughness falls again. These two points are after irradiating 75 min and 180 min. These are the irradiation times used in 2.1.4. There is a

third small peak visible after 135 min irradiation time, but just at a scanning size of 20 µm. T-distribution says, that this point is also relevant.

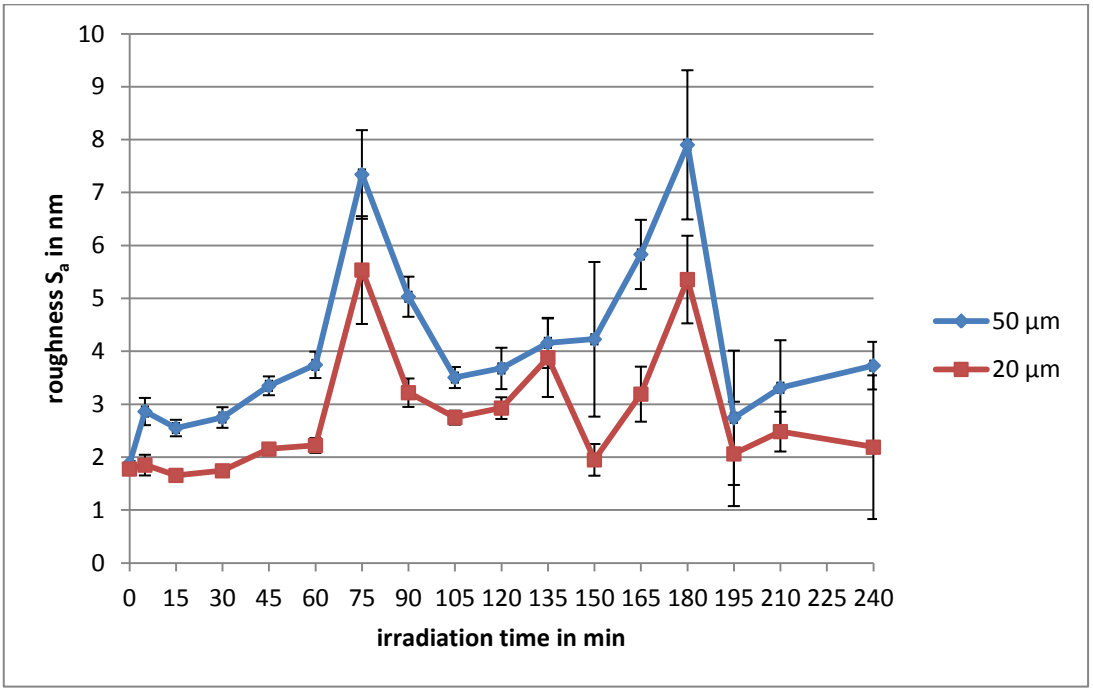

figure 35: Roughness S_a measured with the AFM software Nova. For measuring two different sizes of the picture were used. T-distribution was used with a plausibility of 90%.

3.1.2 Measurement with histograms

The histograms in figure 36 and figure 37 show height profiles for non irradiated and 180 min irradiated samples. For the other irradiation times histograms were also made, but because the result was always the same it was relinquished to show.

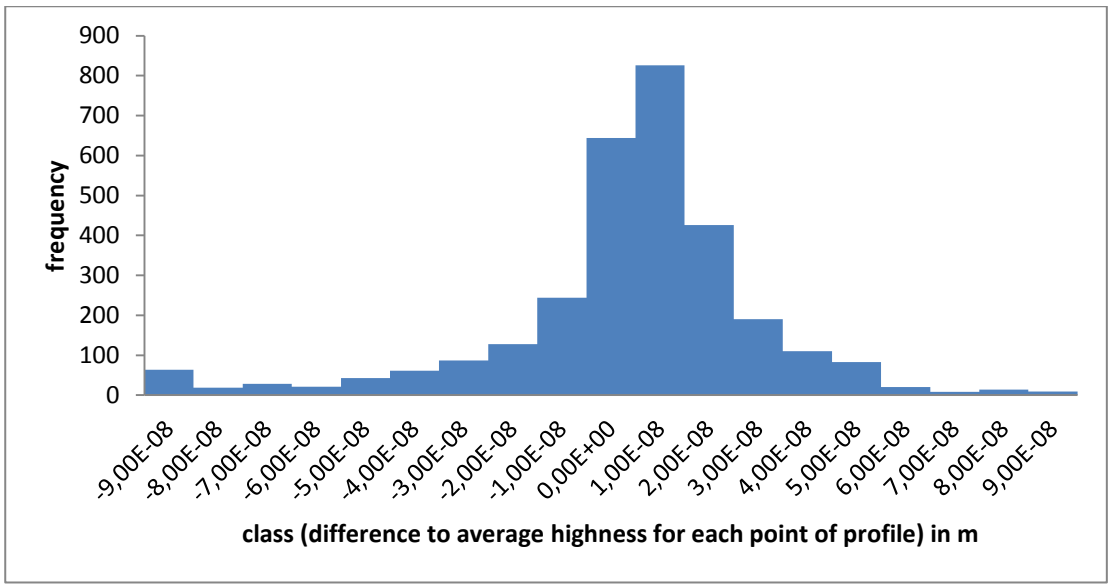

figure 36 : Histogram for 0 min irradiation time. Height profile was taken and average of this profile was subtracted from the value. For these values two pictures were taken and from each pictures three height lines.

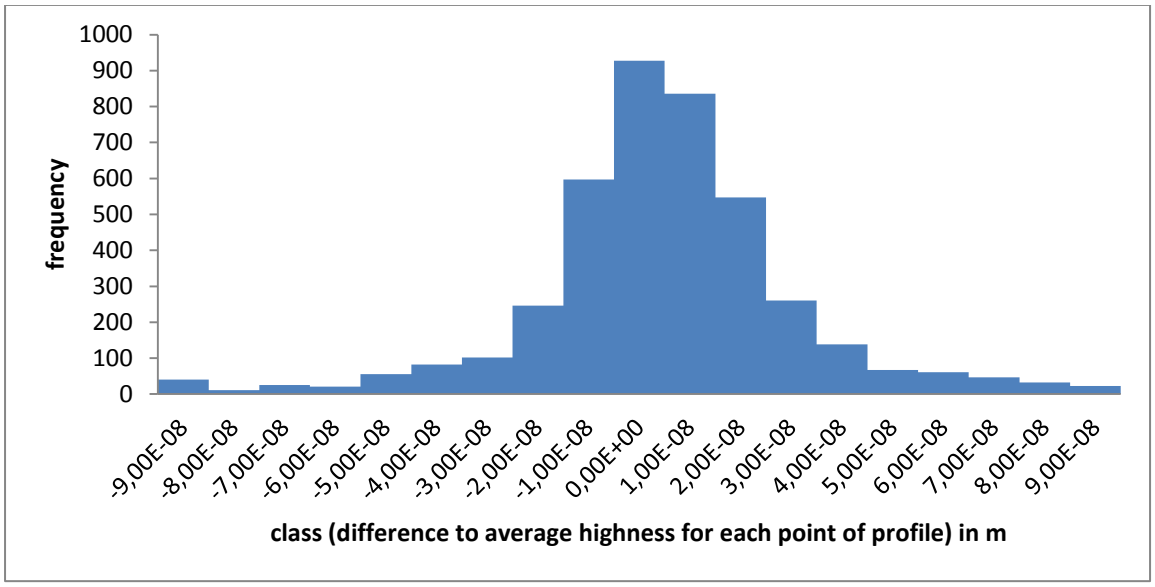

figure 37: Histogram for 180 min irradiation time. Height profile was taken and average of this profile was subtracted from the value. For these values two pictures were taken and from each pictures three height lines.

figure 38 shows quotient of M/D for all histograms, which was calculated with formulas of 2.1.3.2. Here the problem is, that quality of measurement is very bad. There are peaks after an irradiation time of 15 min, 45 min, 120 min and 195 min.

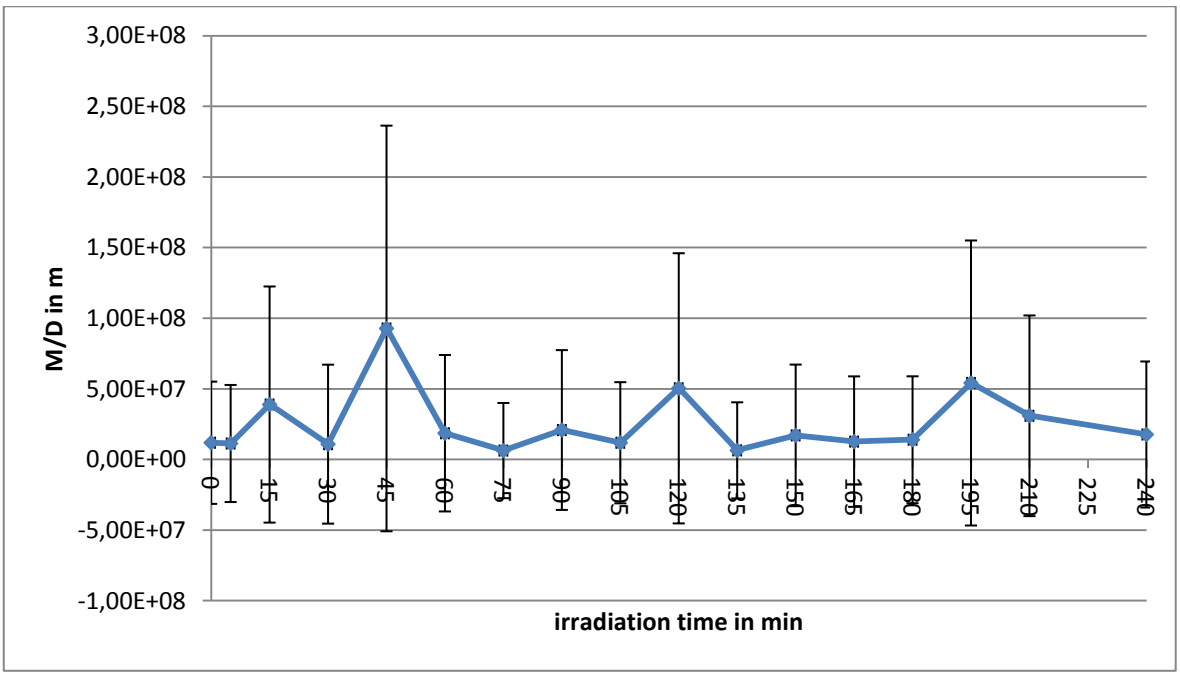

figure 38: Roughness M/D calculated with histograms. T-Distribution was used for plausibility control (90 %).

3.1.3 Measurement with force-distance curves

In the figure 39 angle α of force-distance curve is shown when tip lands and lifts. Angle of lifting force-distance curve is smaller in general, but it is not possible to get more information by showing both curves. So in the following diagrams just angle for landing curve was used.

There is a big minimum of angle α after 180 min of irradiation and a small one after 15 min. These minima mean a higher roughness.

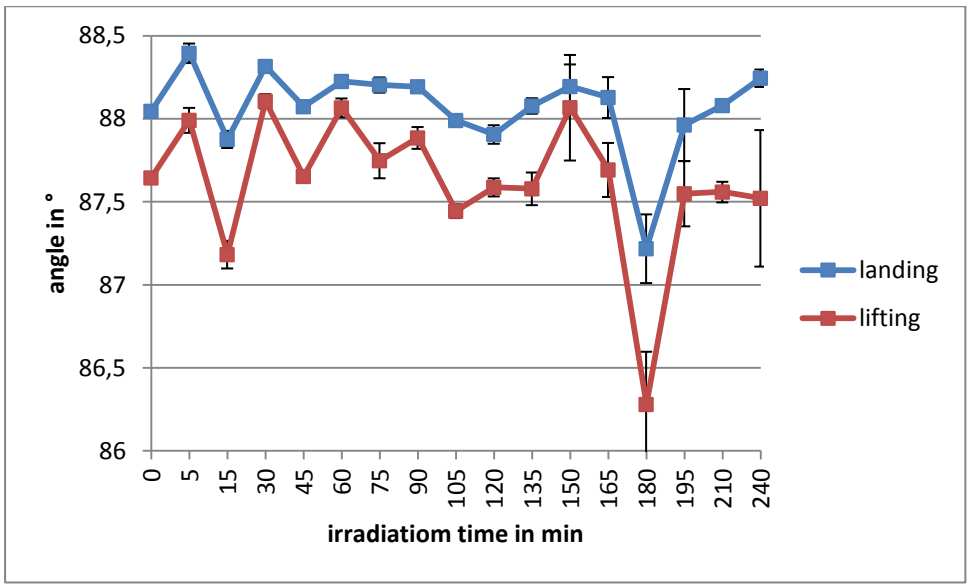

figure 39: Roughness measured with force-distance for landing and lifting. T-Distribution (90%) was used.

3.2 Storage

3.2.1 Room conditions

At the figure 40 temperature and humidity of the storage room are shown. Conditions were measure at the same time every day.

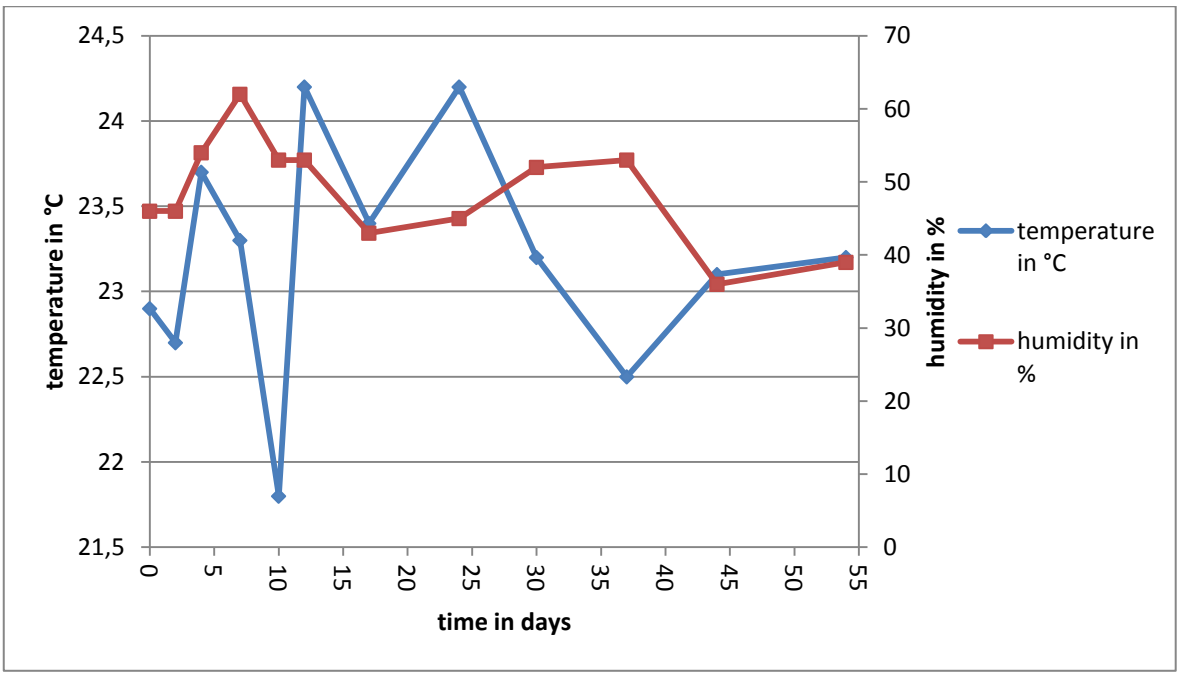

figure 40: temperature and humidity in the storage room.

3.2.2 Measurement with the AFM software

Firstly it was necessary to look, if pure not irradiated PMMA changes roughness while storage in air and in glass. As it can be seen in figure 41 roughness rises in the first 12 days and then it stays constant, where PMMA stored in glass had a bigger roughness than when it was stored in air.

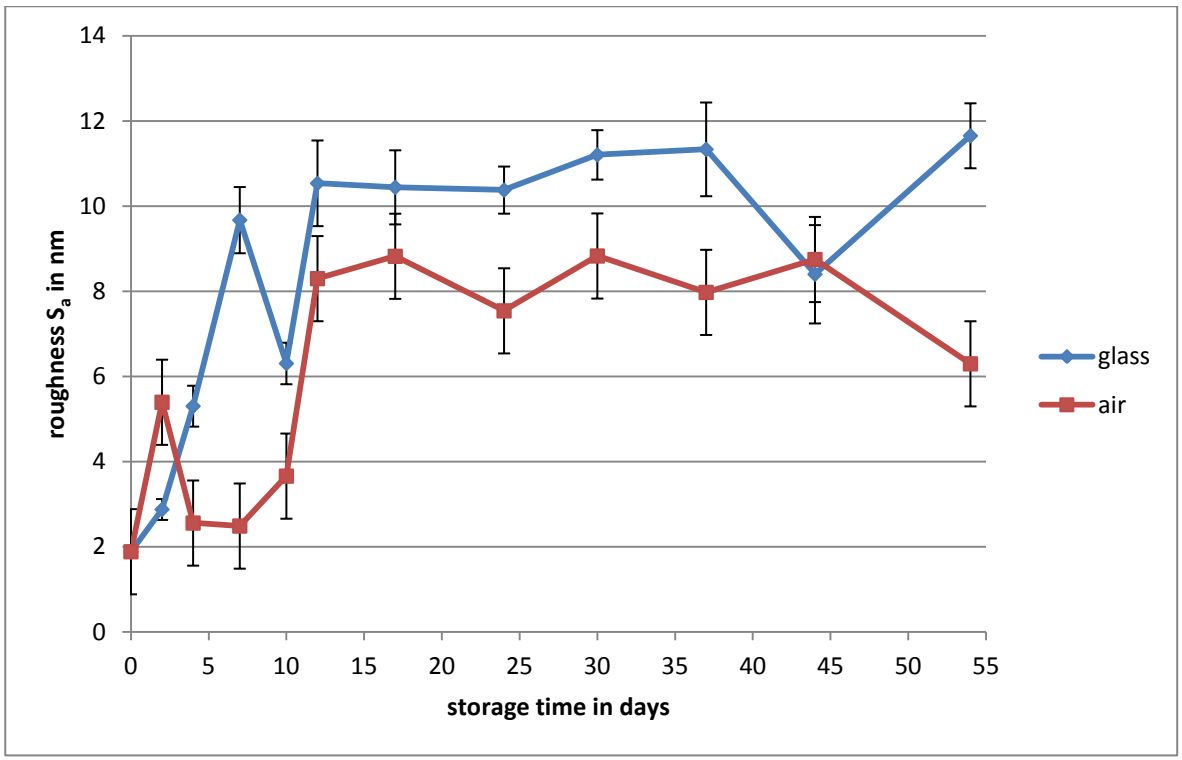

figure 41: Roughness S_a for non-irradiated PMMA stored in air or glass with t-distribution (plausibility: 90%).

For the following measurements difference between irradiated and non-irradiated is much more interesting than absolute values, because influence of irradiation should be observed. So in figure 42 this difference was pointed out for 75 min irradiated samples and in figure 43 for an irradiation time of 180 min.

It is very good to see, that in the first two days roughness falls to beginning level and then there is an oscillation, for an irradiation time of 180 min more than for 75 min. After 15 days roughness is no changing anymore, especially for 180 min for air it takes a longer time in air. After that time roughness is as big as before irradiation.

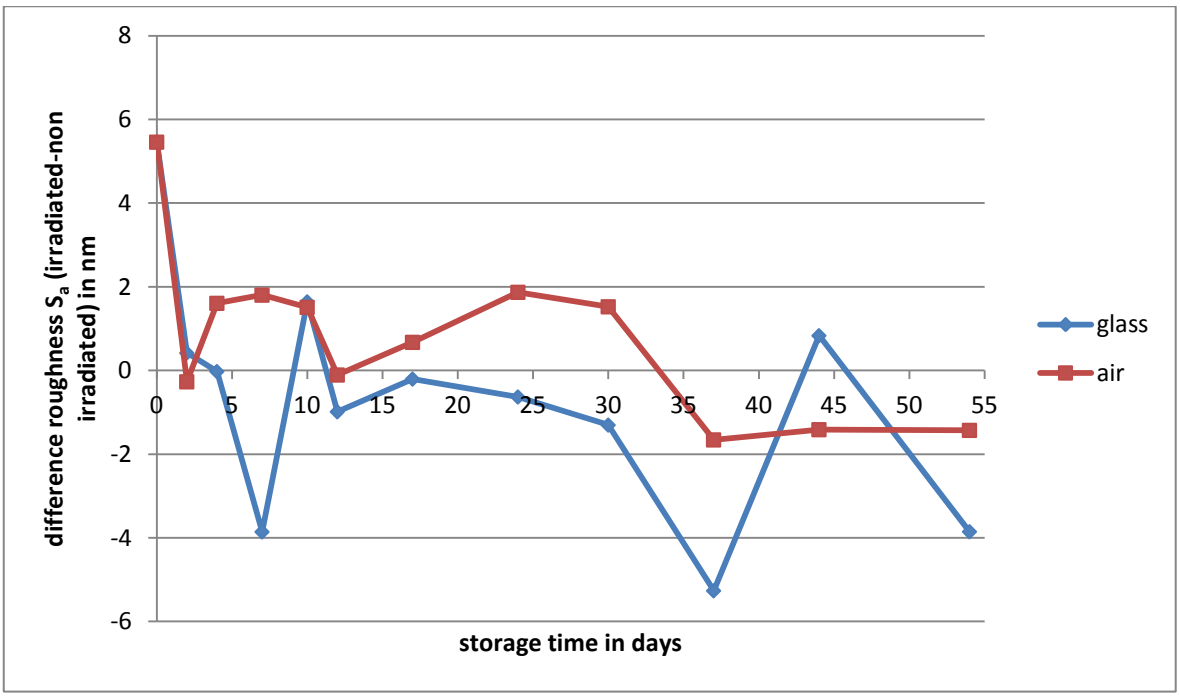

figure 42: Diagram like figure 41 for 75 min irradiation.

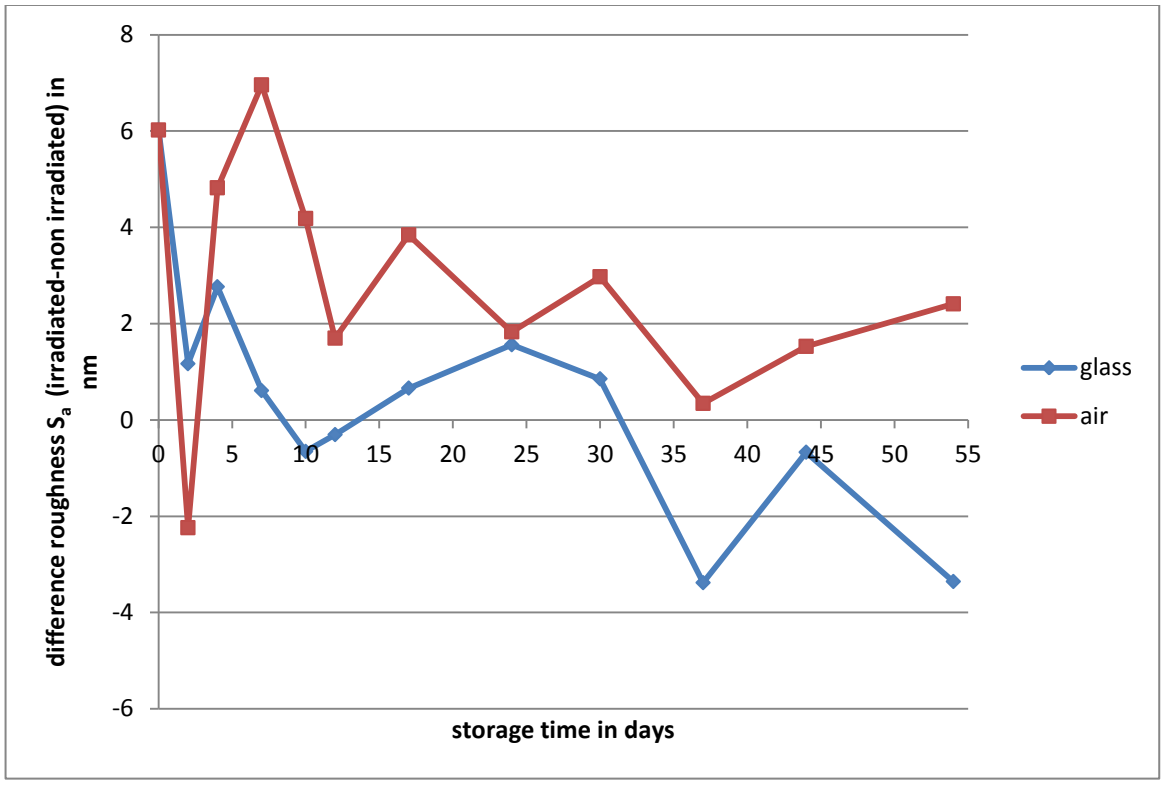

figure 43: figure 44: Diagram like figure 41 for 180 min irradiation.

3.2.3 Measurement with histograms

Measurement with histograms also registries changes for the storage of non-irradiated PMMA independent if it was stored in glass or in air. Firstly there is a rise, but after 20 days M/D, and so roughness stays constant, what can be seen in figure 45 for air and in figure 46 for glass.

Roughness changes more quickly in the case of 180 min irradiated sample than in non-irradiated case. Most quickly and with highest roughness is the sample, which was irradiated 75 min.

The problem also here is, that t-distribution is bigger than the measure itself, so statistical relevance is not big. Here it was relinquished to present distribution.

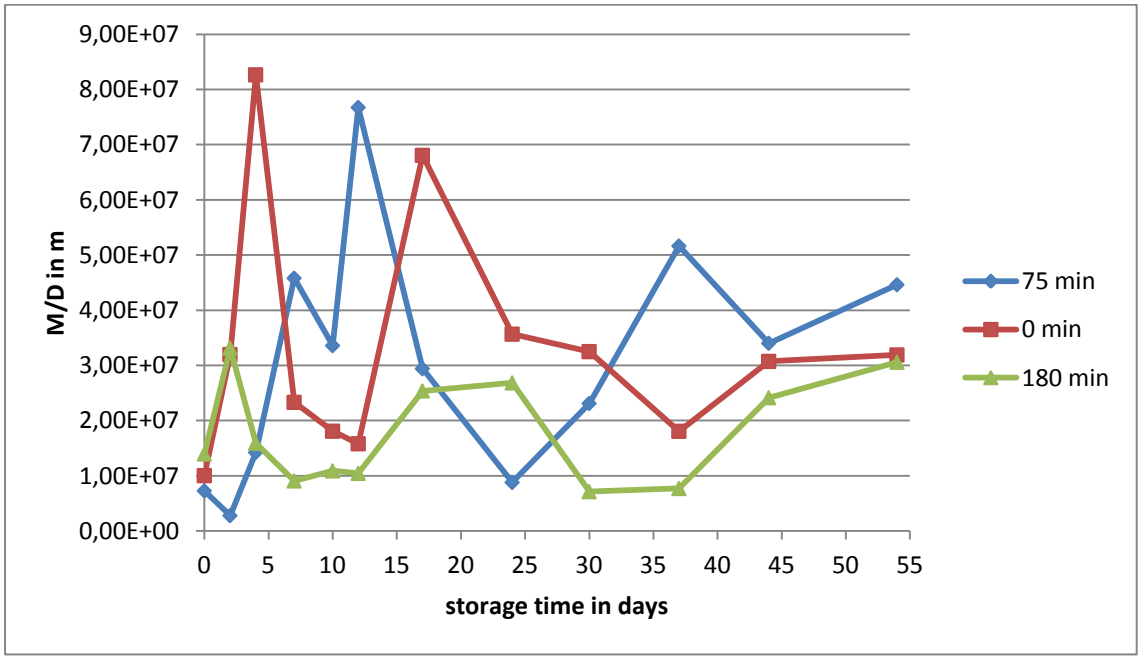

figure 45: Roughness M/D for storage in air.

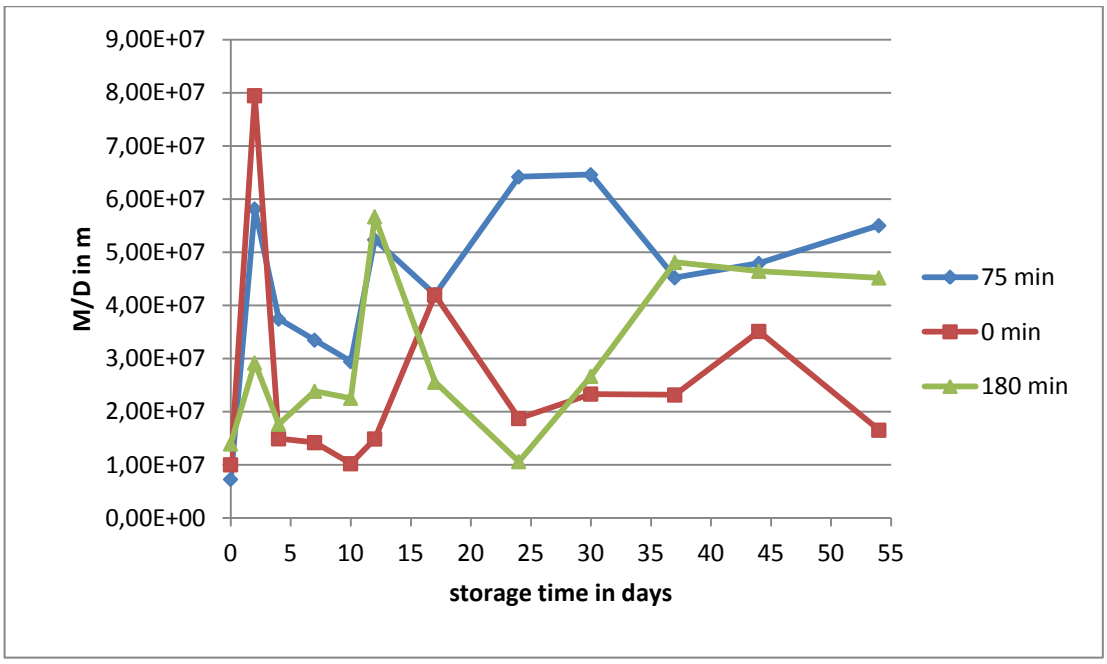

figure 46: Roughness M/D for storage in glass.

Also here difference between irradiated and non-irradiated sample is more interesting and so shown in figure 45 for 75 min of irradiation and in figure 46 for 180 min of irradiation.

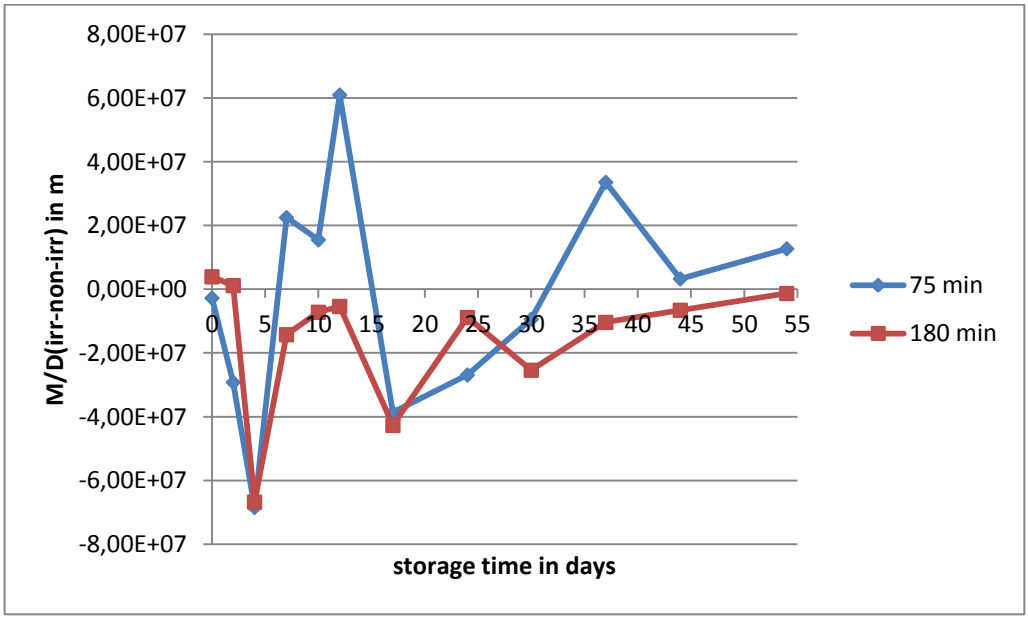

figure 47: Roughness M/D. Difference between irradiated and non-irradiated roughness, stored in air.

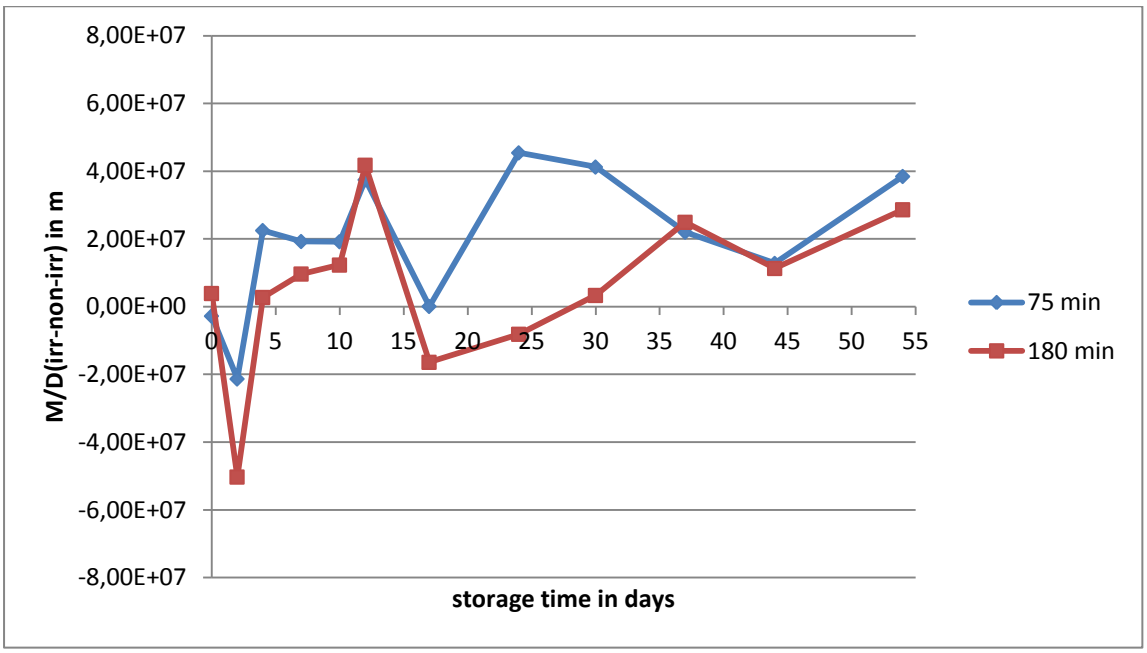

figure 48: Roughness M/D. Difference between irradiated and non-irradiated roughness, stored in glass.

Here directly after irradiation roughness is as big as in non-irradiated case. In the first 4 days for storage in air and in the first 2 days for storage in glass roughness is falling and then it rises again. So also here oscillation is observed.

For storage in air it is good to see, that roughness has got a constant level of roughness, which is roughness of pure PMMA. For storage in glass it seems, that oscillation is not stopping.

3.2.4 Measurement with force-distance curves

In this case it is interesting, that 75 min maximum was not seen by this method. So it is much more interesting to see, if this method registries an influence of irradiation for this irradiation time.

figure 49 and figure 50 show roughness of all samples, irradiated for 75 min, 180 min and non-irradiated. It is good to see, that there is a change of the angle for the non-irradiated sample. Interestingly it is very good to see how non-irradiated sample influences hardness. Sometimes difference between non-irradiated and irradiated sample is extremely small. Also t-distribution is so small, that it couldn´t be seen at the diagram.

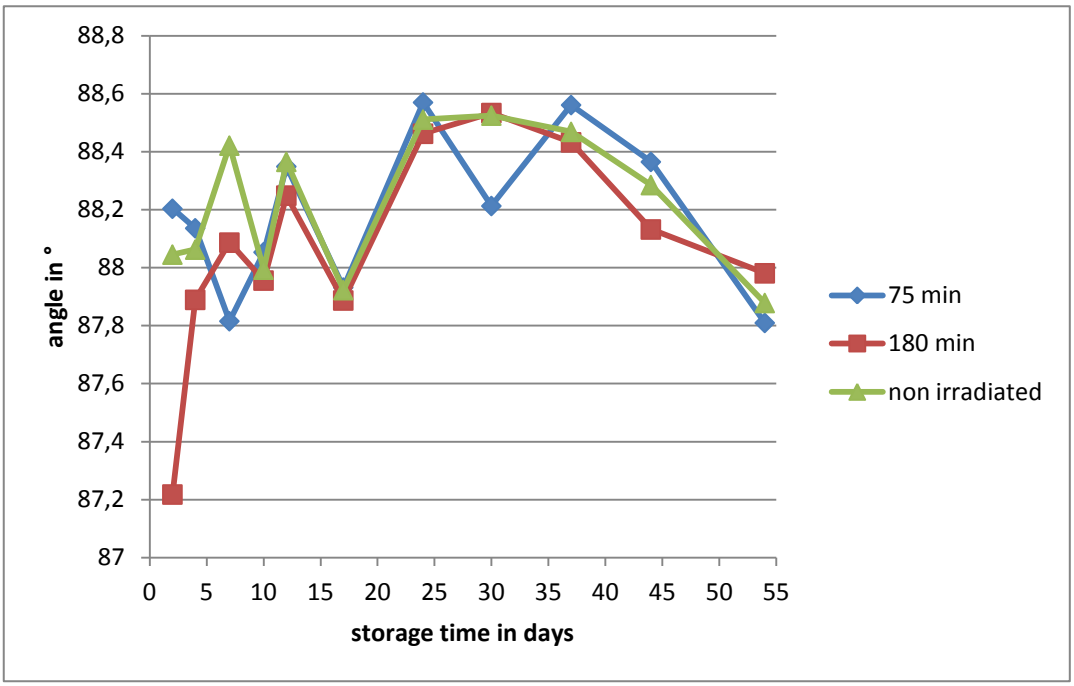

figure 49: Force-distance curve for storage in air.

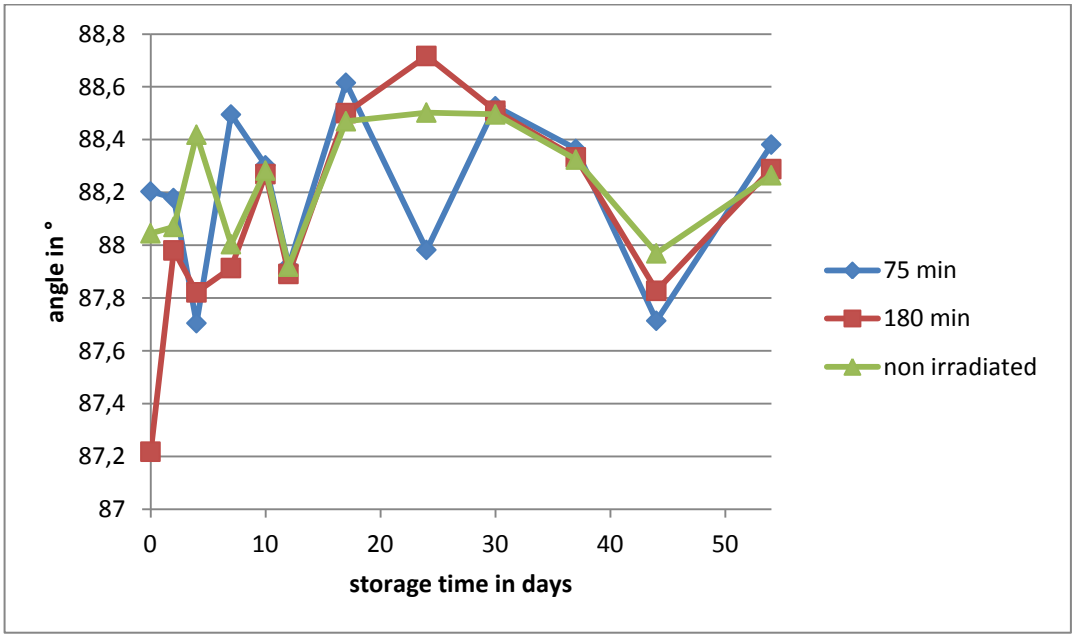

figure 50: Force-distance curve for storage in glass.

There was a peak after an irradiation time of 180 min, but no one after 75 min in 3.1.3, but interestingly this peak is can just be seen at the beginning of the measurement very good. After that there was not such a big difference. To see it better the difference between irradiated and non-irradiated sample was observed in figure 51 and figure 52.

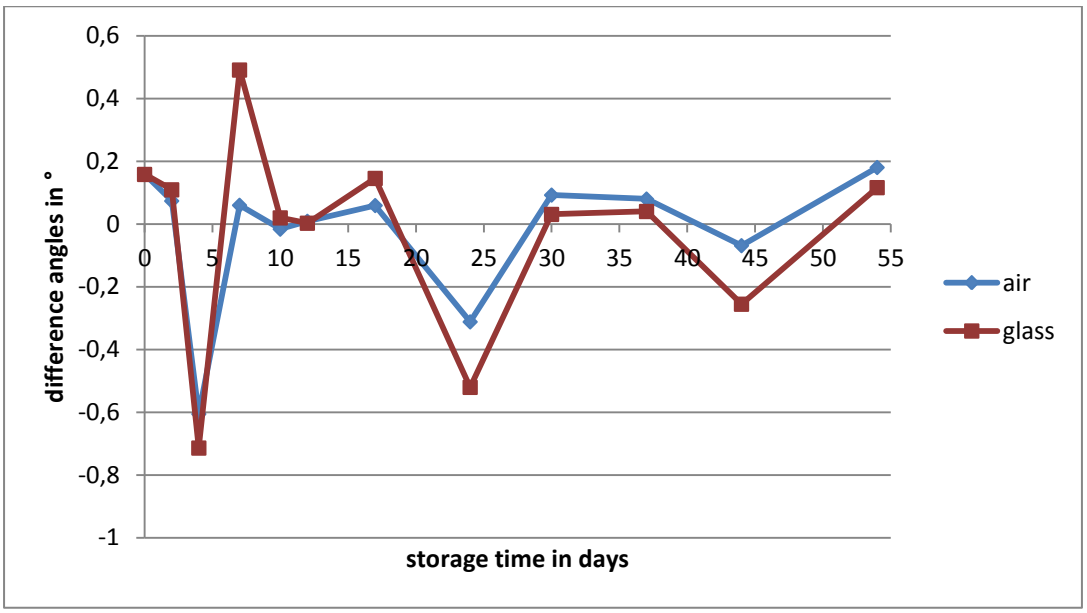

figure 51: Force-distance curve. Here the difference between the 75 min irradiated sample stored in air and stored in glass is shown.

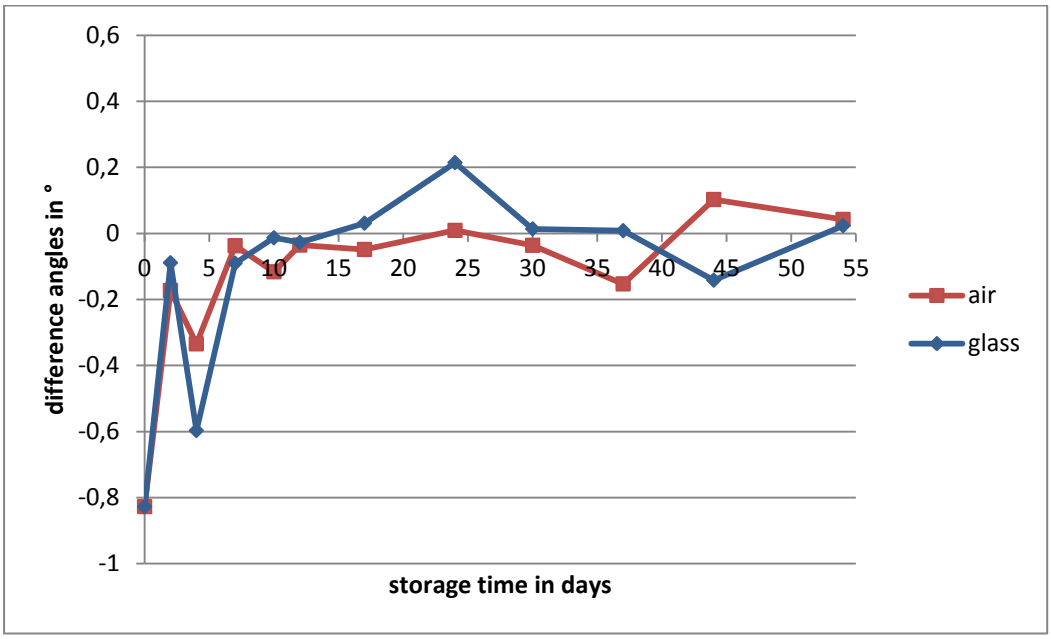

figure 52: Landing force-distance curve. Here the difference between the 180 min irradiated sample stored in air and stored in glass is shown.

4 Discussion

4.1 Irradiation times

4.1.1 Measurement with AFM software

Except for two peaks roughness is constant in irradiation time.

There are two or three peaks, what means, that while irradiation roughness rises suddenly and falls after a short time again. Because of t-distribution it is in all probability (more than 90%), that these peaks exist.

If there is a third peak at 135 min it is not clear, because it was detected with 20x20 µm² picture, but not with 50x50 µm². That peak is statistical relevant for 20x20 µm² picture, so maybe it is a very small peak what could just be detected by the better method. That 20x20 µm² is the better method can be read out of the t-distribution in figure 35

Why did holes and hills appear is not clear. This effect had no influence to average of all pictures, these with holes and these without them.

4.1.2 Measurement with histograms

For the measurement with histograms the same results should be shown as in 4.1.1, because the same pictures are used, just the method of measurement is a different one. Of course quality of measures is not as big as in 4.1.1 because much less data for height were used.

Histograms in figure 36 and figure 37 are symmetric and there is no difference between irradiated and non-irradiated sample visible like it was observed in [SKC2007] that was introduced in 1.5.3.5 . There is a difference between this two histograms, also when it is not visible so clearly, because otherwise M/D would be the same.

All in all there is no increase or decrease of roughness in the observed time, just some peaks like in 4.1.1, but at different places.

There is one peak after 195 min irradiation time. At measurement with software in 3.1.1 there was a peak at 180 min. Because 195 min is just 12% more than 180 min and roughness was measured in 15 min steps it can be seen as the same peak.

If the other peaks at 15 min, 45 min and 120 min are relevant it is hardly to see. T-distribution is very height, so it is possible that these peaks are not statistical relevant. The maximum after 75 min of irradiation, which was detected at 3.1.1 does not appear in this case. So it is also possible, that this peak is shifted to 45 min or 120 min or that these to peaks from here are coextensive with 75 min peak.

4.1.3 Measurement with force-distance curves

At the force-distance curve there is just one peak at the 180 min irradiation time. This is the same position like in 3.1.1 and also in 3.1.2 there is a peak in that region.

This peak is statistical, what can be read out of t-distribution. Because measurements are so clear, there has to be a peak.

A second, smaller peak was detected after an irradiation time of 15 min, which is also statistical relevant.

4.1.4 Conclusion for different irradiation times

Roughness stays constant during the irradiation except for the peaks. That is shown in all experiments. A rise of roughness as it was reported in [DSSM2010], [MCJ2012] and [KaCh2009], but dose was much bigger than in the experiment here (introduced in 1.5.3).

In [YTT2005] no change of roughness was observed, only the changes in other values. As this article had said - something changes in the material - that also experiments here show. Conditions were different, so it could be that these chemical changes had an influence to roughness in this experiment, but not in the experiment of the article.

table 2 shows peaks measured with different methods. Discussions about these peaks were done in 4.1.1, 4.1.2 and 4.1.3.

table 2: Peaks of roughness after the irradiation. Peaks were found out with different methods.

Method	Peaks after irradiation time in min			
AFM software		75	(135)	180
Histograms M/D	(15)	(45)	120	195
Force-distance curve	15			180
Result	**Maybe peak**	**Maybe peak**	**Maybe peak**	**Peak**

There is a peak of roughness after 180 min of irradiation time. That means, that for a short time roughness becomes higher and then it falls again. This peak is measured with all of the methods.

With AFM software a second peak after 75 min was measured, which was not measured by the other methods. So it could be, that this peak is a sum out of 45 min and 120 min at M/D measurement, it could also be, that the peak at 75 min was split. Force-distance curve is a very good method with a low deviation, but there this peak was not visible. Maybe this method was not able to measure this peak or in reality this peak does not exist.

Another critical point is after an irradiation time of 135 min. AFM software for 50x50 µm² was to rough to detect this point, which was statistical relevant with 20x20 µm² pictures. Because M/D method took 50x50 µm² pictures, this peak should not be visible, but there is a peak close to that at 120 min. There is no peak for force-distance curve, what could be interpreted at this peak. It could also be, that force at surface is changing with roughness so, that no peak is visible.

For force-distance curve and for M/D there was another statistical peak after 15 min irradiation time, which was not observed by AFM software. It could be, that AFM-software was to rough to see that point. It is also possible, that this point doesn´t exist or that roughness does not change, but forces and so there is a peak and because of the bad distribution of M/D method there is just a randomly peak.

After the 180 min irradiation time of course energy entry was higher than with other peaks, so it is logical, that this peak is detected with every method while other peaks are not so clear. All the other peaks are speculative.

4.2 Storage

4.2.1 Room conditions

In the observed time temperature stays constant and humidity falls 12% on average, but difference between the highest and the lowest humidity level was 25 %.

Thus the temperature has no influence, but there could be an influence of humidity. To measure this influence the experiment has to be repeated, as it was not done.

All the time conditions were measured at the beginning of the measurements in the morning. Because people were in the room and room was heated conditions changed. These influences were minimized by scanning samples always in the same order.

4.2.2 Measurement with AFM software

There is a change roughness for non-irradiated samples in the first 12 days. Before storage PMMA was sold in foils, which were removed before storage time began. Because of oxygen, dust or other substances in atmosphere it is believable, that roughness rises. Another point is, that samples were put under AFM and back to storage and so roughness can also rise. Because roughness rises just for the first 12 days the last effect wound have a big influence.

In the first two days roughness falls to beginning level in two days, so peaks, which were observed in 3.1.1 are not stabile. What happens after that it is not clear. For an irradiation time of 75 min and storage in air roughness seems to stay constant, because values are very small. When there is no influence of irradiation after 2 days values should be randomly spread over and under line of non-irradiated PMMA, but it is not. Values are in waves, so one value seems to influence the other value. So there could be an oscillation. For storage in glass this oscillation is also visible at the same values.

Because for 180 min roughness also falls and rises again it is unclear, if that, what was described is really happening. After a few days roughness also falls. So it is unclear what is happening, but oscillation is probable.

A significant difference between storage in glass and in air was not observed.

4.2.3 Measurement with histograms

For measurement with histograms roughness does not rise in general, but it has got very big peaks. Because of the big distribution it could be, that these are not statistical. It was not possible to see a rise or a fall. It is interesting, that 180 min irradiated PMMA is more or less constant, while non-irradiated and 75 min irradiated samples are changing roughness much more.

Here it is important to know, that at irradiation times of 75 min and 180 min there was no rise of roughness, what can be seen in figure 38. So for irradiated samples roughness is as big as pure PMMA at the beginning. Also here a fall in the first 2 days was observed. So after 2 days of storage roughness of irradiated PMMA was lower than roughness of non-irradiated PMMA. After that roughness rises again and until day 12 there are some peaks so also this method says that an oscillation could happen. Later roughness is more constant. Because of the high t-distribution it is not possible to say, if this level is a bit higher than roughness of non-irradiated PMMA or if roughness is as big as non-irradiated PMMA.

4.2.4 Measurement with the force-distance curves

Here just 180 min irradiated sample had a higher roughness, 75 min irradiated sample had the same roughness like non-irradiated material at the beginning of measurement.

After just two days roughness of 180 min irradiated PMMA falls so, that there is not a big difference between roughness anymore. It is good to see, that oscillation happen in non-irradiated case but also in irradiated case for the first 12 days. Difference in roughness between irradiated and non-irradiated sample were also in the first days bigger than later. There is no special day, after which roughness stops oscillating. For 180 min irradiated samples it is after 7 days, for 75 min irradiated sample after 30 days. The reason for that is not known.

4.2.5 Conclusion for storage

The alterations, which were observed in the bachelor thesis [Tru2013] for wettability, are also observed for roughness here. So in the first 2 to 4 days there is a rapid fall of roughness. Then it rises again. After circa 12 days oscillations stop and roughness is the same as for the non-irradiated PMMA. Thus the effect of irradiation is lost after two weeks.

There was no influence of the storage conditions, so it did not matter, if the samples were stored in air or in a Petri plate with a glass cover. Because of the measuring it was necessary to open the Petri plate every second day so it is possible that there is an influence, but it was not big enough for a visible change. After these two days the air was changed.

Because of the alterations , which was observed with all the methods, is the same for the 180 min and 75 min samples, it is assumed that there is a second peak after 75 min, but it is also possible, that oscillation also happens, when there is no peak. For observing a new experiment with an irradiation time of maybe 150 min would be necessary, because there no peak was observed with all of the methods.

5 Outlook

Also for short irradiation times chemical reactions are at the PMMA surface. After these experiments it is still not clear, which reaction it is. Except for wettability and hardness it is not clear, if other physical units are also changing.

There is also a reaction after irradiation that can be observed for more units. Until now it is not clear, if the material changes back into the beginning material or if the material after irradiation and 12 days is a different one. It is not often observed, that roughness alternates. This is another point that should be made clear.

Storage conditions were observed in air and in a Petri dish out of glass, but in it there was also air. So a next experiment would be to look, if something happens when Petri dish is full of water or another fluid. For this experiment this experiments were basics to know, that there is no influence of Petri dish material.

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7 Statement of Authorship

Herewith I declare, that I drew up the present research paper independently and just by using of the listed references and tools.

Passages, which were taken from references word by word or corresponding, are marked as such ones.

This project was not submitted to another exam authority in that or similar form.

Hartenstein, 14th April, 2014

Tabea Schettler